Supporting Information - Deriving the vibronic coupling constants of the cyclopentadienyl radical with density functional theory and G_0W_0

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S1. COMPUTATIONAL DETAILS

A. Range and interval of points used in the fitting of ab initio calculations

We know from symmetry considerations that the first, second, and third order derivatives of the orbital energies for both ψ_θ and ψ_ϵ should be identical to each other along the set of $e_2^{'}$ normal coordinates, Q_θ and Q_ϵ. In addition, as the $V^{(4)}_{e_2^{'}}$ term is zero along Q_ϵ, the fourth order derivative for ψ_θ and ψ_ϵ should be equal only for the Q_ϵ coordinates. Finally, it is not desirable to have a range of points that is too large as anharmonicity effects and the distortion of the degenerate HOMOs become significant far from the parent geometry.

The effect of varying the range and interval of points used to fit the vibronic Hamiltonian was then tested for ν_9 and ν_{10}, with the aim of obtaining fitted derivatives that obey the conditions above as far as reasonably possible. The calculations in this section were carried out at the PBE0/cc-pVTZ level of theory. The results are then given in Tables S1 and S2, with a final range of (-20, 20) a.u. with a interval of 0.2 a.u. between data points.

TABLE S1. Comparison of the i^{th} derivatives of the energies of ψ_θ and ψ_ϵ ($\varepsilon_{\psi_\theta}$ and $\varepsilon_{\psi_\epsilon}$) with respect to the $e_2^{'}$ normal coordinates, Q_θ and Q_ϵ, of ν_9 and ν_{10} as the range of points is varied. The interval of data points was 0.2 a.u. throughout.

		$\nu_9(Q_\theta)$		$\nu_9(Q_\epsilon)$		$\nu_{10}(Q_\theta)$		$\nu_{10}(Q_\epsilon)$	
Range	i	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$
(-20, 20)	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.71E-7	-5.71E-7	-5.71E-7	-5.71E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.31E-10	-7.12E-10	7.21E-10	-7.21E-10	2.33E-9	-2.26E-9	2.29E-9	-2.29E-9
	4	7.36E-12	-1.63E-11	-3.30E-12	-5.78E-12	2.43E-10	-2.41E-10	2.44E-10	2.41E-10
(-15, 15)	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.71E-7	-5.71E-7	-5.71E-7	-5.71E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.29E-10	-7.14E-10	7.22E-10	-7.22E-10	2.33E-9	-2.29E-9	2.30E-9	-2.30E-9
	4	1.57E-11	-2.42E-11	7.69E-13	-9.44E-12	2.51E-10	2.33E-10	2.48E-10	2.37E-10
(-10, 10)	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.72E-7	-5.71E-7	-5.71E-7	-5.70E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.28E-10	-7.17E-10	7.20E-10	-7.20E-10	2.32E-9	-2.31E-9	2.31E-9	-2.31E-9
	4	8.44E-11	-9.37E-11	3.27E-11	-4.24E-11	3.20E-10	1.66E-10	2.82E-10	2.01E-10
(-5, 5)	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.77E-7	-5.65E-7	-5.74E-7	-5.68E-7	-2.43E-6	-2.42E-6	-2.43E-6	-2.43E-6
	3	7.48E-10	-7.27E-10	6.87E-10	-7.01E-10	2.32E-9	-2.31E-9	2.24E-9	-2.24E-9
	4	2.45E-9	-2.52E-9	1.22E-9	-1.32E-9	2.61E-9	-2.18E-9	1.44E-9	-1.06E-9

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TABLE S2. Comparison of the i^{th} derivatives of the energies of ψ_θ and ψ_ϵ ($\varepsilon_{\psi_\theta}$ and $\varepsilon_{\psi_\epsilon}$) with respect to the $e_2^{'}$ normal coordinates, Q_θ and Q_ϵ, of ν_9 and ν_{10} as the interval of points is varied. The range of data points was (-20, 20) a.u. throughout.

		$\nu_9(Q_\theta)$		$\nu_9(Q_\epsilon)$		$\nu_{10}(Q_\theta)$		$\nu_{10}(Q_\epsilon)$	
Interval	i	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$
0.2	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.71E-7	-5.71E-7	-5.71E-7	-5.71E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.31E-10	-7.12E-10	7.21E-10	-7.21E-10	2.33E-9	-2.26E-9	2.29E-9	-2.29E-9
	4	7.36E-12	-1.63E-11	-3.30E-12	-5.78E-12	2.43E-10	-2.41E-10	2.44E-10	2.41E-10
0.4	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.71E-7	-5.71E-7	-5.71E-7	-5.71E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.31E-10	-7.12E-10	7.22E-10	-7.21E-10	2.33E-9	-2.26E-9	2.29E-9	-2.29E-9
	4	9.74E-12	-1.87E-11	-2.02E-12	-7.04E-12	2.46E-10	2.38E-10	2.45E-10	2.40E-10
0.8	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.72E-7	-5.71E-7	-5.71E-7	-5.70E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.31E-10	-7.12E-10	7.21E-10	-7.21E-10	2.33E-9	-2.26E-9	2.29E-9	-2.29E-9
	4	1.43E-11	-2.33E-11	2.39E-13	-9.38E-12	2.50E-10	2.34E-10	2.47E-10	2.38E-10
2.0	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.72E-7	-5.71E-7	-5.71E-7	-5.70E-7	-2.43E-6	-2.42E-6	-2.43E-6	-2.43E-6
	3	7.31E-10	-7.11E-10	7.22E-10	-7.22E-10	2.33E-9	-2.26E-9	2.29E-9	-2.29E-9
	4	2.61E-11	-3.52E-11	6.20E-12	-1.52E-11	2.62E-10	-2.22E-10	2.53E-10	2.32E-10

We also carried out a set of *ab initio* calculations using Gaussian16 for comparison (Table S3). The 'Superfine' and 'NoSymm' keywords were used in these calculations. The resultant fitted derivatives were found to be in good agreement with the values obtained by fitting the CP2K results. However, the Gaussian16 .fchk file prints orbital energies up to 9 significant figures, which was increased to 11 significant figures in our CP2K calculations, which could explain why the fourth order derivatives for the two programs differ from each other.

TABLE S3. Comparison of the i^{th} derivatives of the energies of ψ_θ and ψ_ϵ ($\varepsilon_{\psi_\theta}$ and $\varepsilon_{\psi_\epsilon}$) with respect to the $e_2^{'}$ normal coordinates, Q_θ and Q_ϵ, of ν_9 and ν_{10} as determined using Gaussian16 and CP2K6.1

		$\nu_9(Q_\theta)$		$\nu_9(Q_\epsilon)$		$\nu_{10}(Q_\theta)$		$\nu_{10}(Q_\epsilon)$	
Program	i	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\theta}$	$\varepsilon_{\psi_\epsilon}$
CP2K6.1	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.71E-7	-5.71E-7	-5.71E-7	-5.71E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.31E-10	-7.12E-10	7.21E-10	-7.21E-10	2.33E-9	-2.26E-9	2.29E-9	-2.29E-9
	4	7.36E-12	-1.63E-11	-3.30E-12	-5.78E-12	2.43E-10	-2.41E-10	2.44E-10	2.41E-10
Gaussian16	1	1.68E-4	-1.68E-4	1.68E-4	-1.68E-4	2.72E-4	-2.72E-4	2.72E-4	-2.72E-4
	2	-5.71E-7	-5.72E-7	-5.71E-7	-5.71E-7	-2.43E-6	-2.43E-6	-2.43E-6	-2.43E-6
	3	7.36E-10	-7.09E-10	7.25E-10	-7.25E-10	2.34E-9	-2.23E-9	2.28E-9	-2.28E-9
	4	1.26E-11	-1.13E-11	7.79E-12	5.22E-12	3.11E-10	3.12E-10	3.22E-10	3.19E-10

B. Derivatives using PBE optimised structure and vibrational normal modes

The derivatives of the energies of ψ_θ ($\varepsilon_{\psi_\theta}$) with respect to the $e_2^{'}$ normal modes obtained using the PBE and PBE0 optimised structures and normal modes are given in Table S4. The calculations for this comparison were carried out using Gaussian16.

TABLE S4. Comparison of the i^{th} derivatives of the energies of ψ_θ, $\varepsilon_{\psi_\theta}$, with respect to the $e_2^{'}$ normal modes obtained using the PBE and PBE0 optimised structures and normal modes. Only the derivatives of $\varepsilon_{\psi_\theta}$ with respect to Q_θ are given as the derivatives to Q_θ and Q_ϵ are effectively equal (See Tables S1 and S2). Similarly, we omit the derivatives of $\varepsilon_{\psi_\epsilon}$ here.

Method	i	ν_9	ν_{10}	ν_{11}	ν_{12}
PBE // PBE	1	1.62E-4	2.42E-4	4.99E-4	2.57E-5
	2	-6.26E-7	-2.29E-6	-3.12E-6	-5.89E-6
	3	1.25E-9	1.97E-9	4.65E-10	9.90E-10
	4	-2.38E-11	2.67E-10	1.05E-9	1.17E-9
PBE0 // PBE	1	1.62E-4	2.52E-4	5.04E-4	2.57E-5
	2	-6.47E-7	-2.33E-6	-3.22E-6	-5.95E-6
	3	1.23E-9	2.03E-9	5.03E-10	1.14E-9
	4	-2.50E-11	2.40E-10	1.01E-9	1.14E-9

C. IP-tuning of range-separation parameter

The aim of IP-tuning is to reduce the difference between the negative energies of the HOMO and IP of the molecule, calculated as the difference between the N and $N-1$ electron system, where N is the number of electrons in the molecule. To do so, an error function J^2 is defined by

$$J^2 = [\varepsilon_{HOMO}(N) + IP(N)]^2 + [\varepsilon_{HOMO}(N+1) + IP(N+1)]^2 \tag{1}$$

where

$$IP(N) = E(N-1) - E(N). \tag{2}$$

ε_{HOMO} is the energy of the HOMO, while E refers to the SCF energy of the molecule with N or $N-1$ electrons. Using the PBE0 optimised geometry of the cyclopentadienyl anion, single point LC-ωPBE and ULC-ωPBE calculations of the anion, doubly charged anion and neutral radical were carried out with Gaussian16 as the range-separation parameter γ is varied from 0.15 to 0.45 Bohr^{-1} to determine the value of J^2 with respect to γ. A fourth order polynomial is then fitted to J^2, and the value of γ at which J^2 is at a minimum is then the IP-tuned value of γ. This was found to be 0.2673 Bohr^{-1} in the case of the cyclopentadienyl anion.

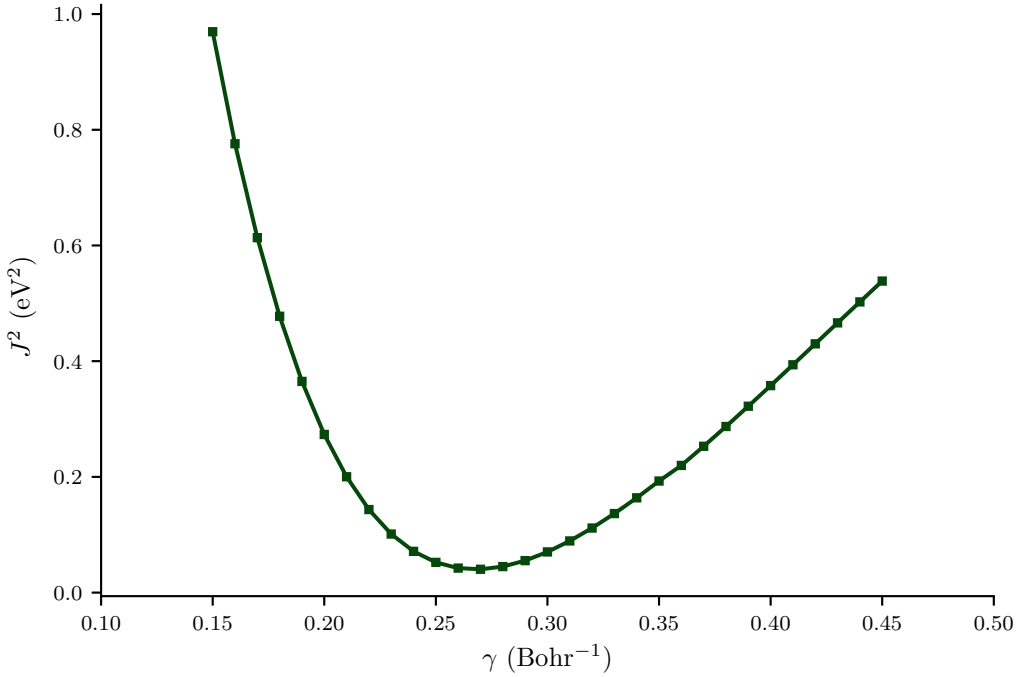

FIG. S1. Plot of the error function J^2 against γ for the tuning of the LC-ωPBE functional for the cyclopentadienyl anion. The cc-pVTZ basis set was used.

D. Numerical convergence of results with respect to CP2K input parameters

The results of varying the CP2K input parameters on calculations with the cyclopentadienyl anion are summarised in Tables S5 to S12. The calculations in this section were carried out at the PBE0/cc-pVTZ level of theory.

The source code of CP2K6.1 was also modified slightly to print out the G_0W_0 quasiparticle energies in atomic units at a higher level of precision.

TABLE S5. Testing of MGRID options in CP2K: NGRIDS. All units are in hartrees.The options 'CUTOFF 800' and 'REL_CUTOFF 70' were used here

NGRIDS	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
4	-193.348187878301	0.00852047060	0.00852068779
5	-193.348187878301	0.00852047060	0.00852068779
6	-193.348187878301	0.00852047060	0.00852068779

TABLE S6. Testing of MGRID options in CP2K: REL_CUTOFF. All units are in hartrees. The options 'CUTOFF 800', 'NGRIDS 4', 'MAX_SCF 1' were used here

REL_CUTOFF	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
40	-197.946475741104	-0.01901385432	-0.01901360531
60	-197.946475903967	-0.01901386040	-0.01901361132
70	-197.946475904275	-0.01901386047	-0.01901361139
80	-197.946475904321	-0.01901386045	-0.01901361137
90	-197.946475904317	-0.01901386046	-0.01901361138
100	-197.946475904317	-0.01901386046	-0.01901361138

TABLE S7. Testing of MGRID options in CP2K: CUTOFF. All units are in hartrees. The options 'REL_CUTOFF 70', 'NGRIDS 4' and 'MAX_SCF 1' were used here

CUTOFF	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
280	-197.946475416107	-0.01901382696	-0.01901357622
600	-197.946475917718	-0.01901386227	-0.01901361318
700	-197.946475916527	-0.01901386131	-0.01901361215
800	-197.946475904275	-0.01901386047	-0.01901361139
900	-197.946475915049	-0.01901386124	-0.01901361210
1000	-197.946475904159	-0.01901386103	-0.01901361190

TABLE S8. Testing of QS options in CP2K: EPS_DEFAULT. All units are in hartrees. The options 'REL_CUTOFF 70', 'NGRIDS 4', 'CUTOFF 800', 'EPS_SCF 1.0E-11' were used here

EPS_DEFAULT	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
1.0E-10	-193.348187878301	0.00852047060	0.00852068779
1.0E-11	-193.348187253519	0.00852061302	0.00852083021
1.0E-12	-193.348187212157	0.00852061807	0.00852083527
1.0E-13	-193.348187212727	0.00852061821	0.00852083541
1.0E-14	-193.348187215850	0.00852061840	0.00852083560
1.0E-15	-193.348187216111	0.00852061839	0.00852083559

TABLE S9. Testing of QS options in CP2K: EPS_PGF_ORB. All units are in hartrees. The options 'REL_CUTOFF 70', 'NGRIDS 4', 'CUTOFF 800', 'EPS_SCF 1.0E-11' were used here

EPS_PGF_ORB	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
-5	-193.348187878301	0.00852047060	0.00852068779
-6	-193.348187212124	0.00852061791	0.00852083510
-7	-193.348187215822	0.00852061823	0.00852083543
-8	-193.348187215998	0.00852061822	0.00852083542
-9	-193.348187216036	0.00852061823	0.00852083542
-10	-193.348187216037	0.00852061823	0.00852083542
-11	-193.348187216037	0.00852061823	0.00852083542
-12	-193.348187216037	0.00852061823	0.00852083542
-13	-193.348187216037	0.00852061823	0.00852083542
-14	-193.348187216037	0.00852061823	0.00852083542
-15	-193.348187216037	0.00852061823	0.00852083542

TABLE S10. Testing of QS options in CP2K: EPSFIT. All units are in hartrees. The options 'REL_CUTOFF 70', 'NGRIDS 4', 'CUTOFF 800', 'EPS_SCF 1.0E-11' were used here

EPSFIT	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
-4	-193.348187878301	0.00852047060	0.00852068779
-5	-193.348236871844	0.00851803568	0.00851825287
-6	-193.348271248561	0.00851634423	0.00851656143
-7	-193.348544275942	0.00851158472	0.00851180194
-8	-193.348746476497	0.00850902452	0.00850924177
-9	-193.348979049519	0.00850882068	0.00850912824
-10	-193.349150540839	0.00850619534	0.00850650295
-11	-193.349294341294	0.00850411224	0.00850441988
-12	-193.349423433444	0.00850231545	0.00850262313

TABLE S11. Testing of integration grids in CP2K: RADIAL_GRID. All units are in hartrees. The options 'REL_CUTOFF 70', 'NGRIDS 4', 'CUTOFF 800', 'EPS_SCF 1.0E-11', 'LEBEDEV_GRID 700' were used here

RADIAL_GRID	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
50	-193.348198711026	0.00852021420	0.00852043140
75	-193.348187890424	0.00852047511	0.00852069231
100	-193.348187877049	0.00852047081	0.00852068801
125	-193.348187877595	0.00852047069	0.00852068788
150	-193.348187877603	0.00852047069	0.00852068788
175	-193.348187877600	0.00852047069	0.00852068788
200	-193.348187877603	0.00852047069	0.00852068788

TABLE S12. Testing of integration grids in CP2K: LEBEDEV_GRID. All units are in hartrees. The options 'REL_CUTOFF 70', 'NGRIDS 4', 'CUTOFF 800', 'EPS_SCF 1.0E-11', 'RADIAL_GRID 150' were used here

LEBEDEV_GRID	E	$\varepsilon_{\psi_\epsilon}$	$\varepsilon_{\psi_\epsilon}$
100	-193.348187877694	0.00852047059	0.00852068781
200	-193.348187877602	0.00852047069	0.00852068788
300	-193.348187877602	0.00852047069	0.00852068788
400	-193.348187877602	0.00852047069	0.00852068788
500	-193.348187877603	0.00852047069	0.00852068788
590	-193.348187877603	0.00852047069	0.00852068788
600	-193.348187877603	0.00852047069	0.00852068788
700	-193.348187877603	0.00852047069	0.00852068788
800	-193.348187877603	0.00852047069	0.00852068788

A sample CP2K6.1 input file is given below:

```
&GLOBAL
  RUN_TYPE     Energy
  PROJECT      Cyclopentadienyl
  PRINT_LEVEL  Medium
&END GLOBAL

&FORCE_EVAL
  METHOD QS

  &DFT
    BASIS_SET_FILE_NAME DUNNING_BASIS_SETS
    CHARGE -1
    &PRINT
      &MO
        Eigenvalues
        NDigits 11
        Occupation_Numbers
      &END MO
    &END PRINT

    &MGRID
      NGRIDS 4
      CUTOFF 800
      REL_CUTOFF 70
    &END MGRID

    &QS
      METHOD GAPW
      EPS_DEFAULT 1.0E-14
      EPS_PGF_ORB 1.0E-7
      EPSFIT 1.0E-8
    &END QS

    &POISSON
      PERIODIC NONE
      PSOLVER MT
    &END

    &SCF
      EPS_SCF 1.0E-11
      SCF_GUESS RESTART
      MAX_SCF 200
    &END SCF

    &XC
      &XC_FUNCTIONAL PBE
      &END XC_FUNCTIONAL
    &END XC
  &END DFT

  &SUBSYS
    &CELL
      ABC 20.0 20.0 20.0
      PERIODIC NONE
    &END CELL

    &TOPOLOGY
```

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      COORD_FILE_FORMAT XYZ
      COORD_FILE_NAME cyclopentadienyl.xyz

      &CENTER_COORDINATES
      &END CENTER_COORDINATES
    &END TOPOLOGY

    &KIND H
      BASIS_SET cc-pVTZ
      POTENTIAL ALL
      LEBEDEV_GRID 100
      RADIAL_GRID 100
    &END KIND

    &KIND C
      BASIS_SET cc-pVTZ
      POTENTIAL ALL
      LEBEDEV_GRID 100
      RADIAL_GRID 100
    &END KIND
  &END SUBSYS

&END FORCE_EVAL
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E. Fitting of energies

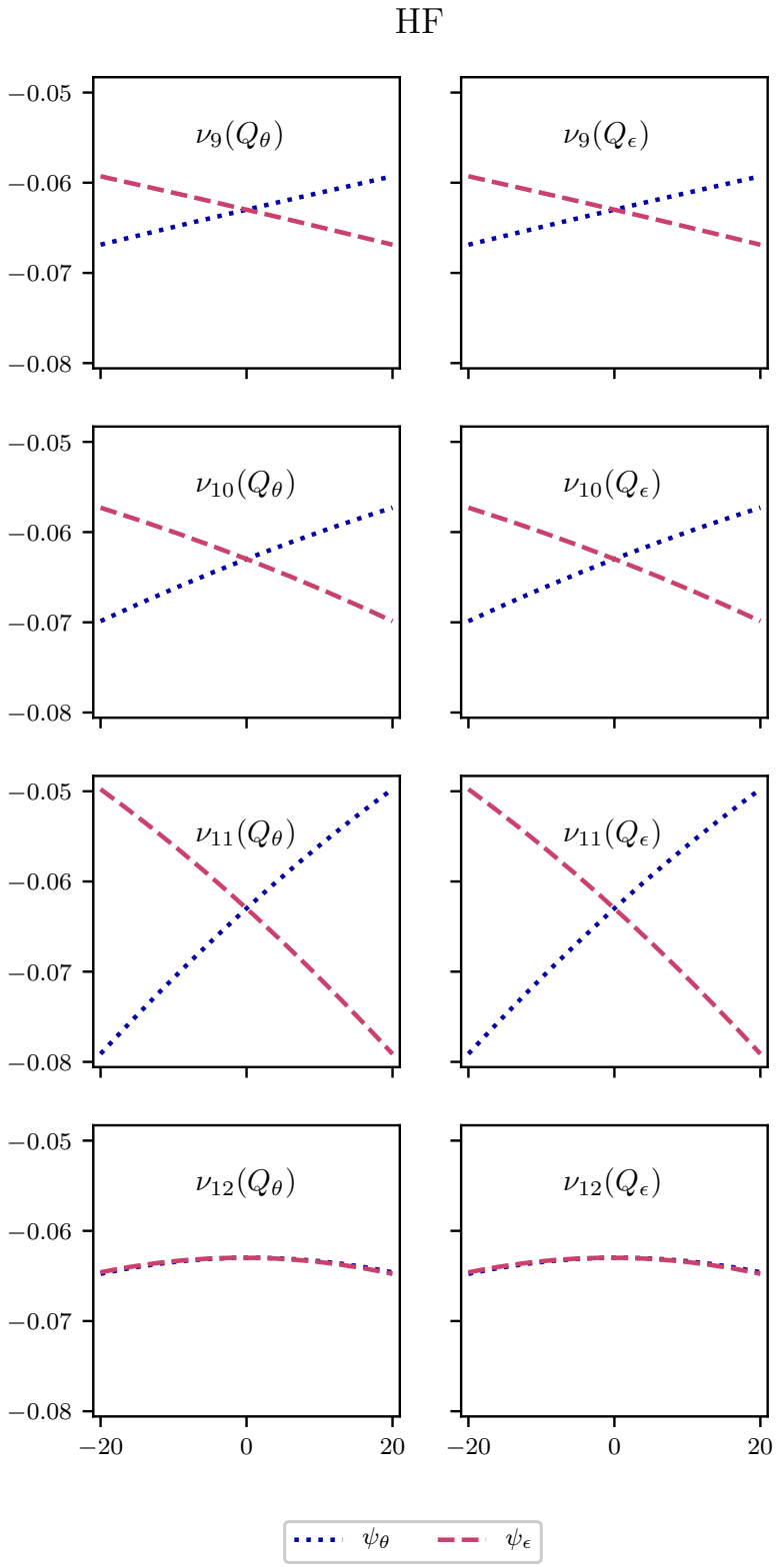

FIG. S2. HF energies of ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

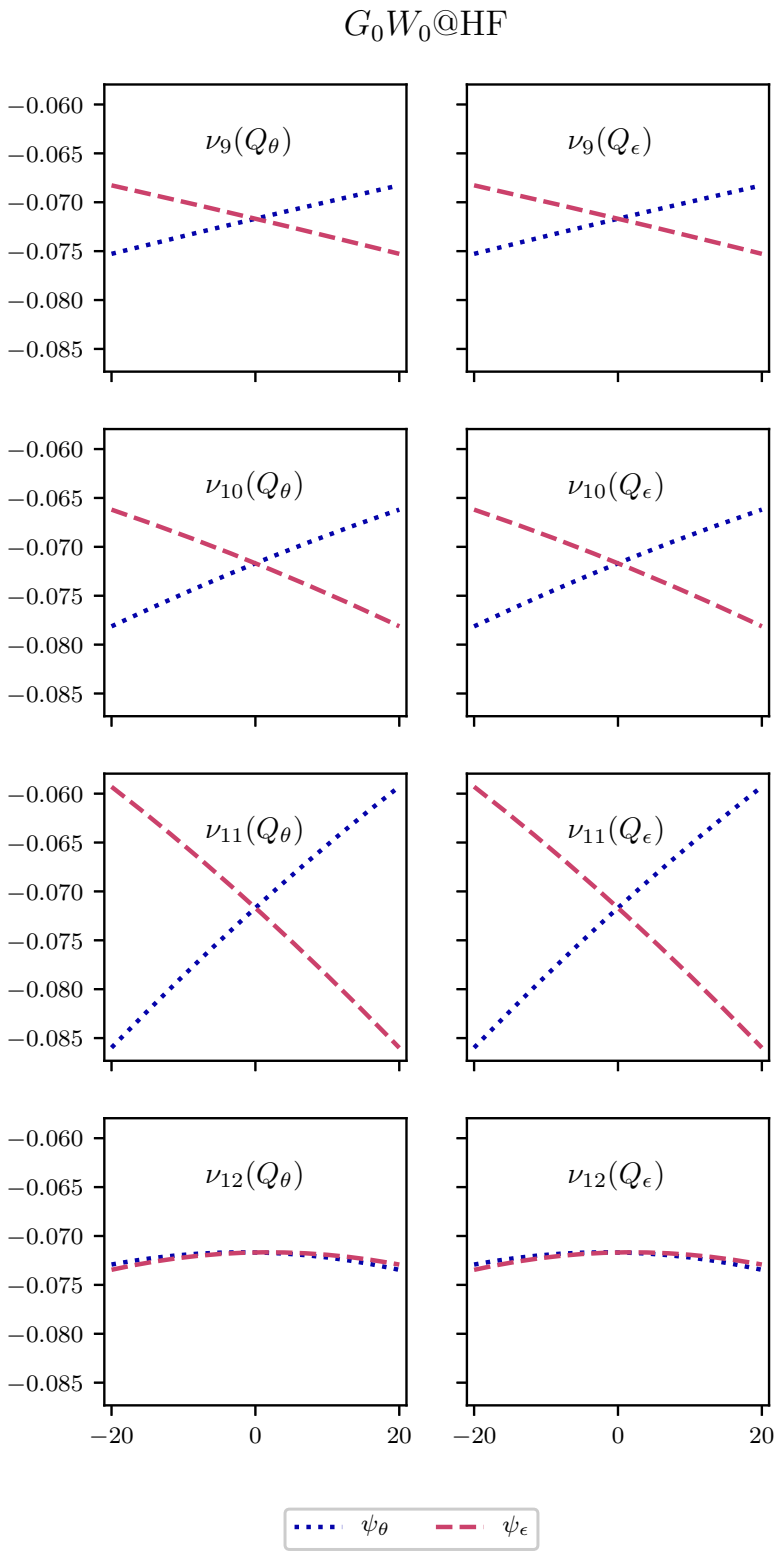

FIG. S3. G_0W_0@HF quasiparticle energies for ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

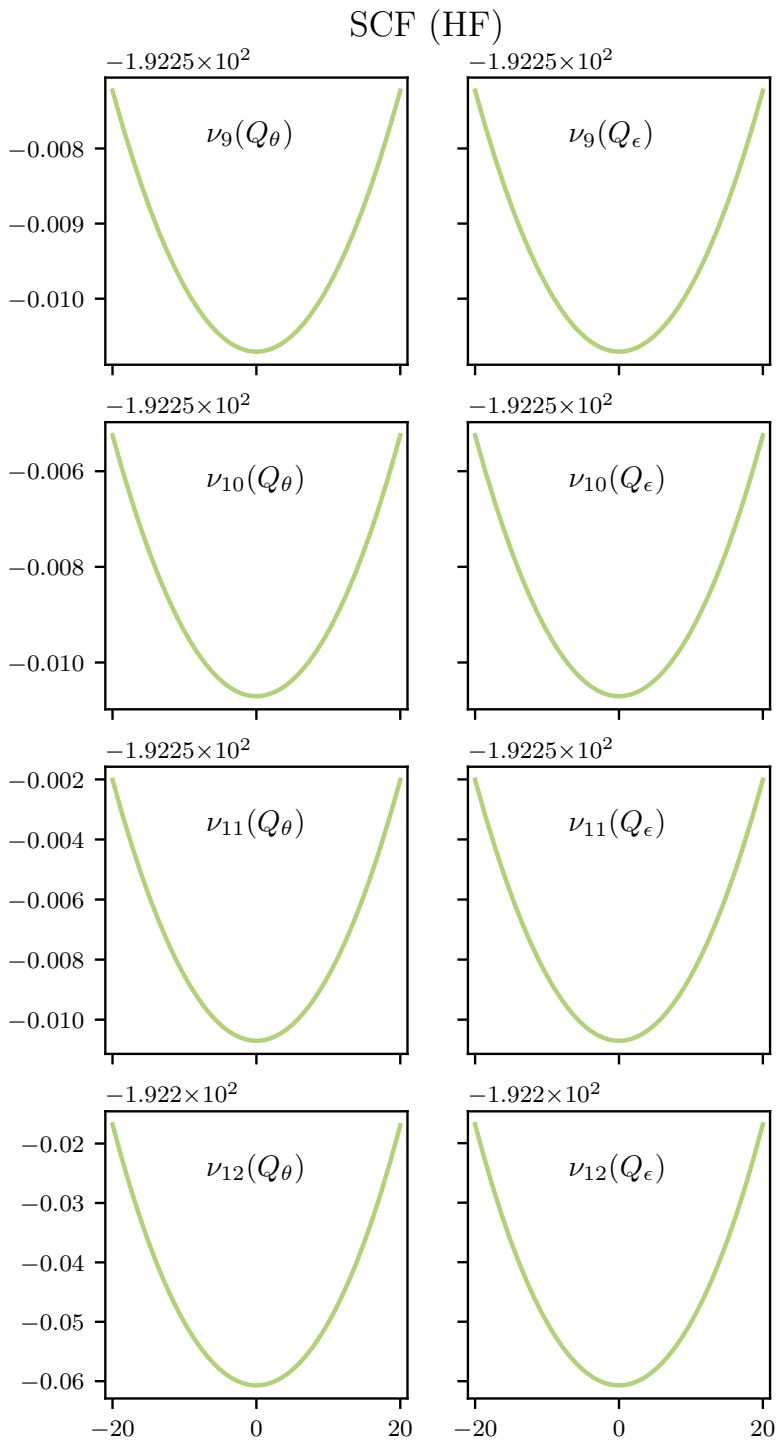

FIG. S4. HF SCF energies with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

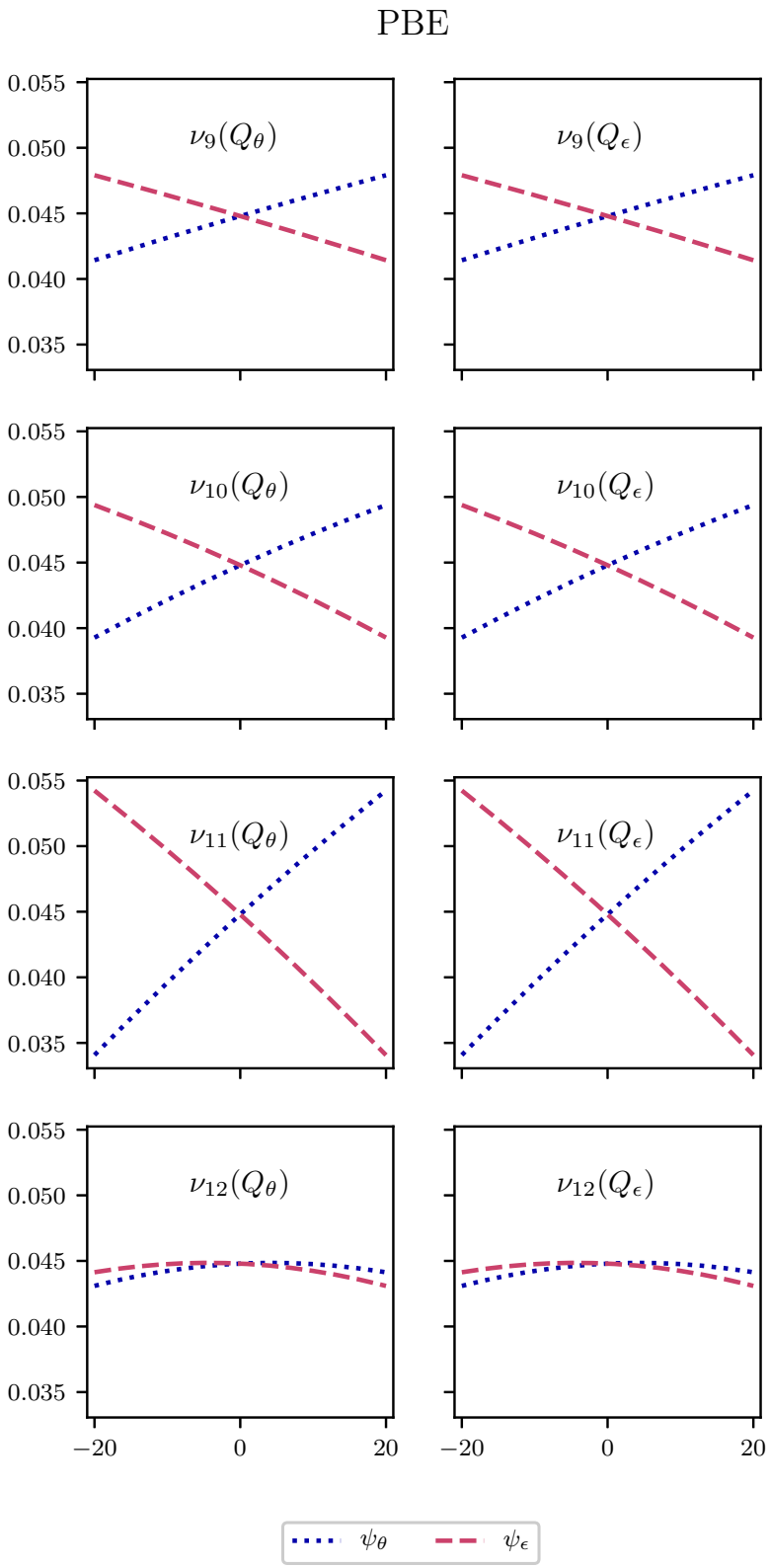

FIG. S5. PBE energies of ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

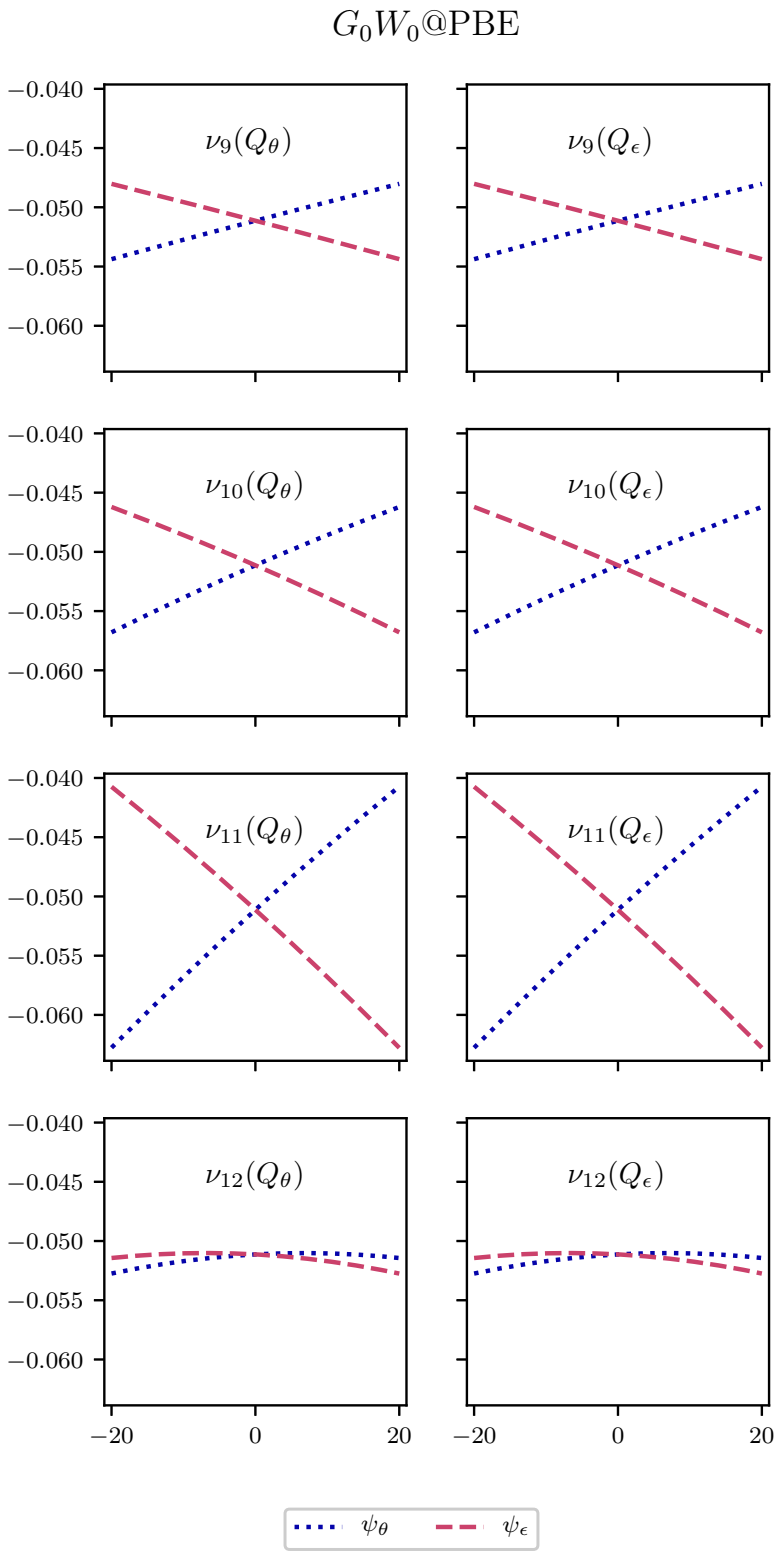

FIG. S6. G_0W_0@PBE quasiparticle energies for ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

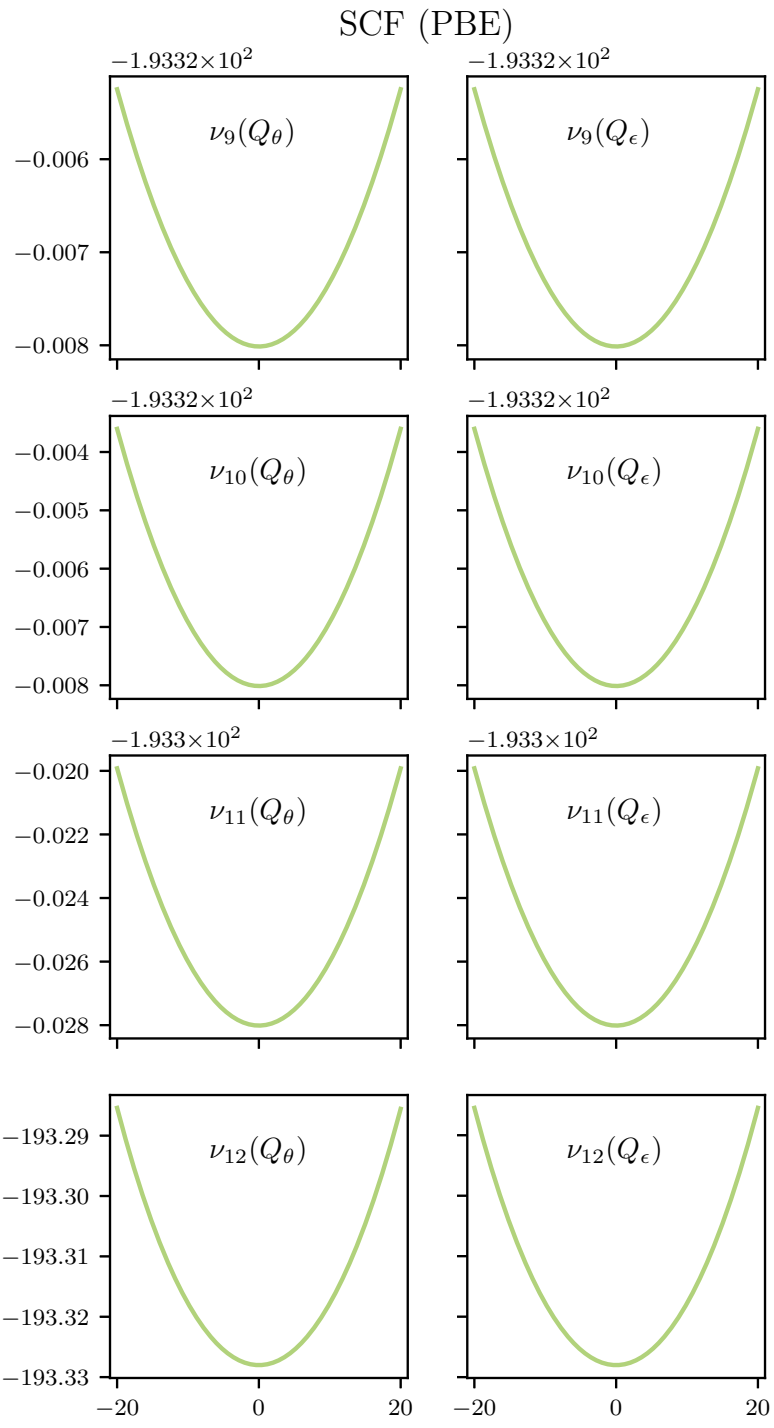

FIG. S7. PBE SCF energies with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

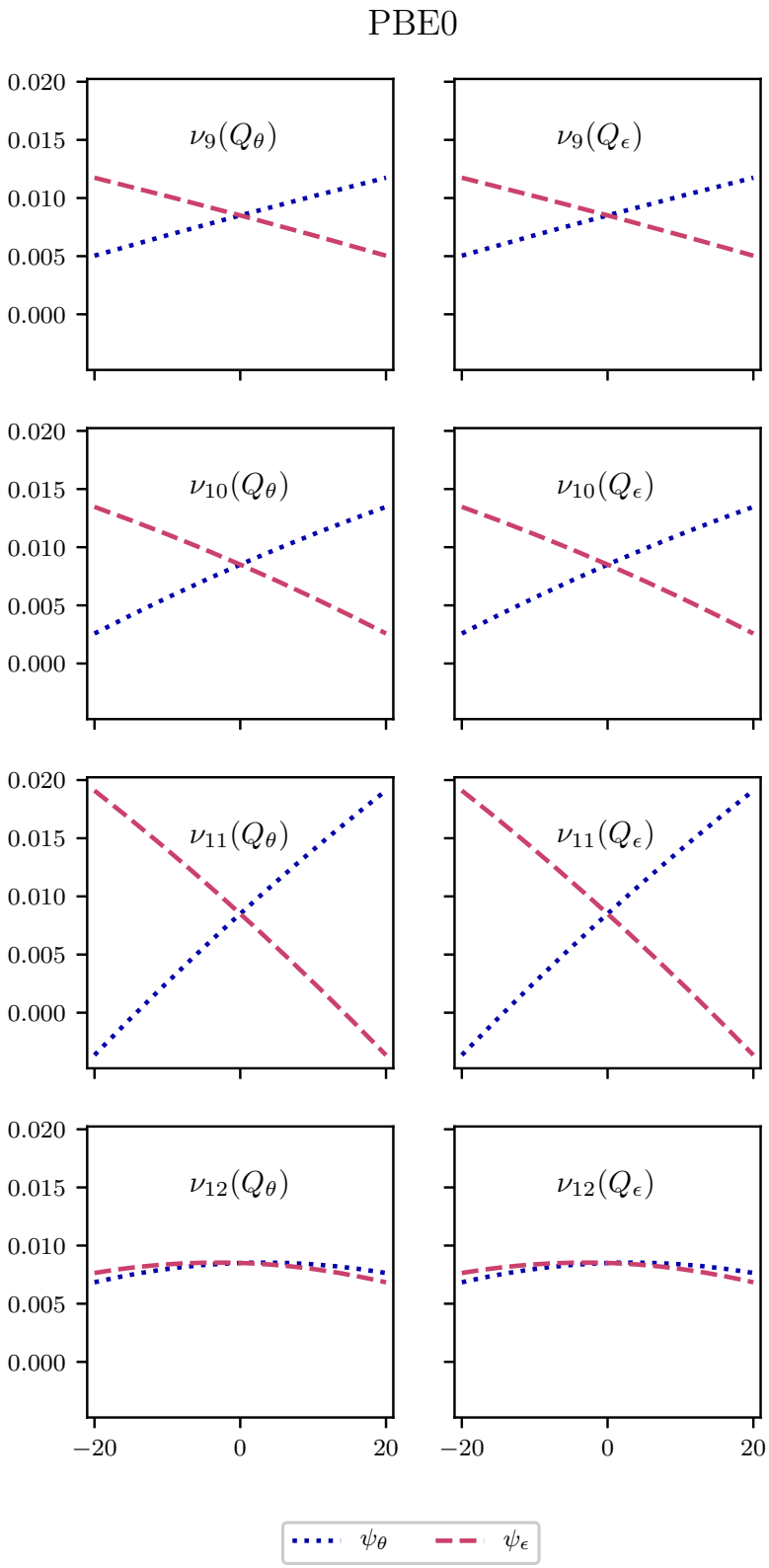

FIG. S8. PBE0 energies of ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

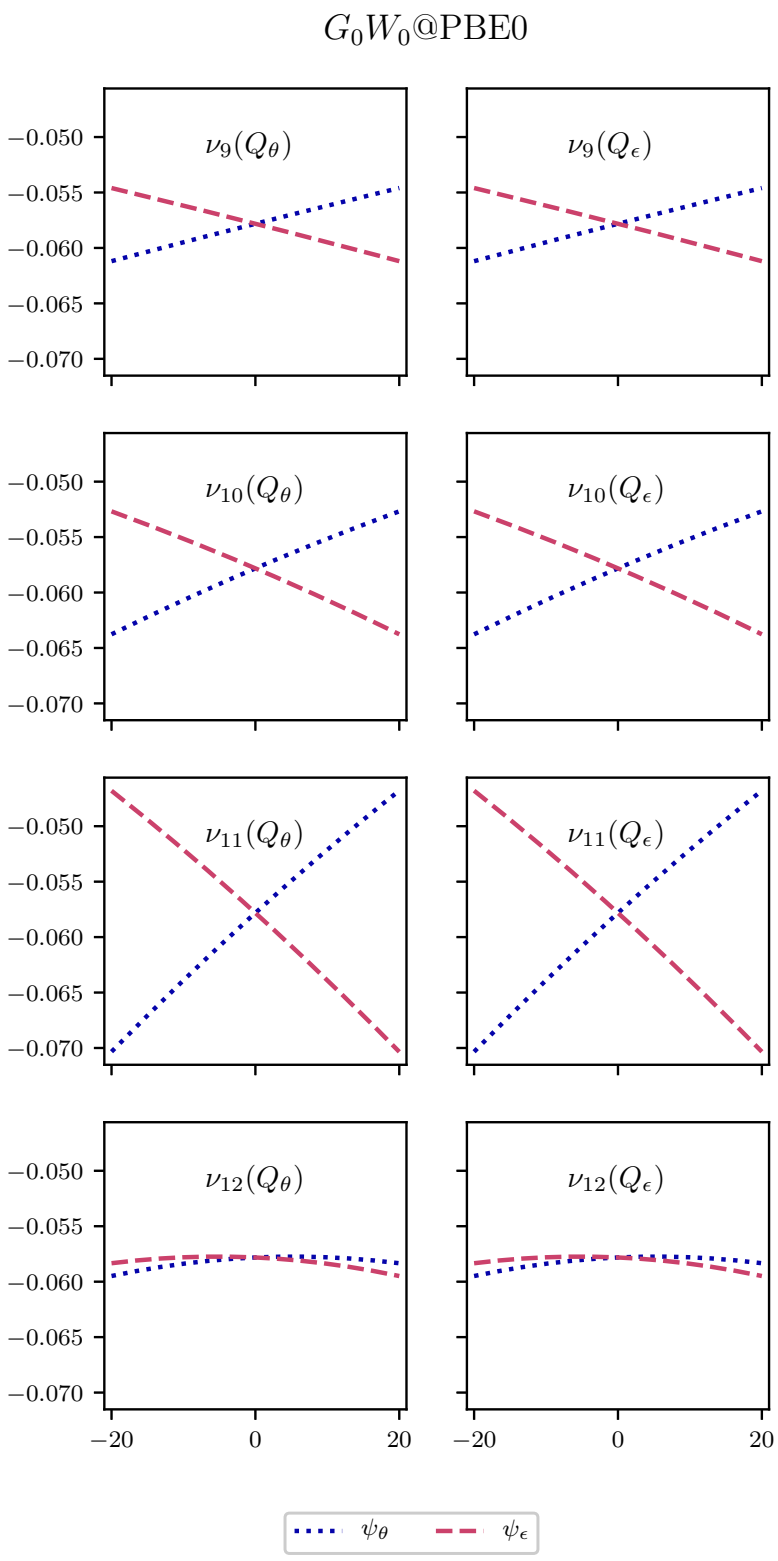

FIG. S9. G_0W_0@PBE0 quasiparticle energies for ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

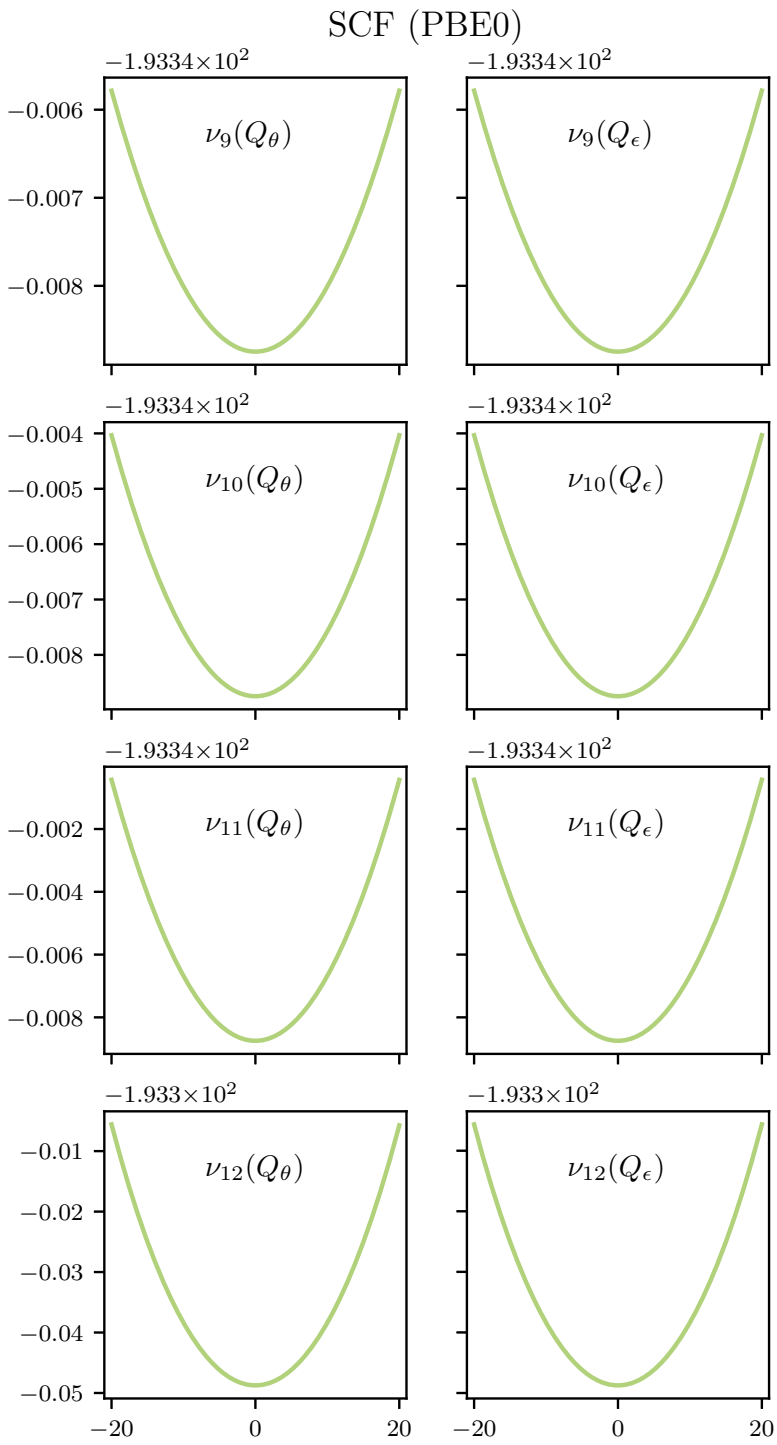

FIG. S10. PBE0 SCF energies with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

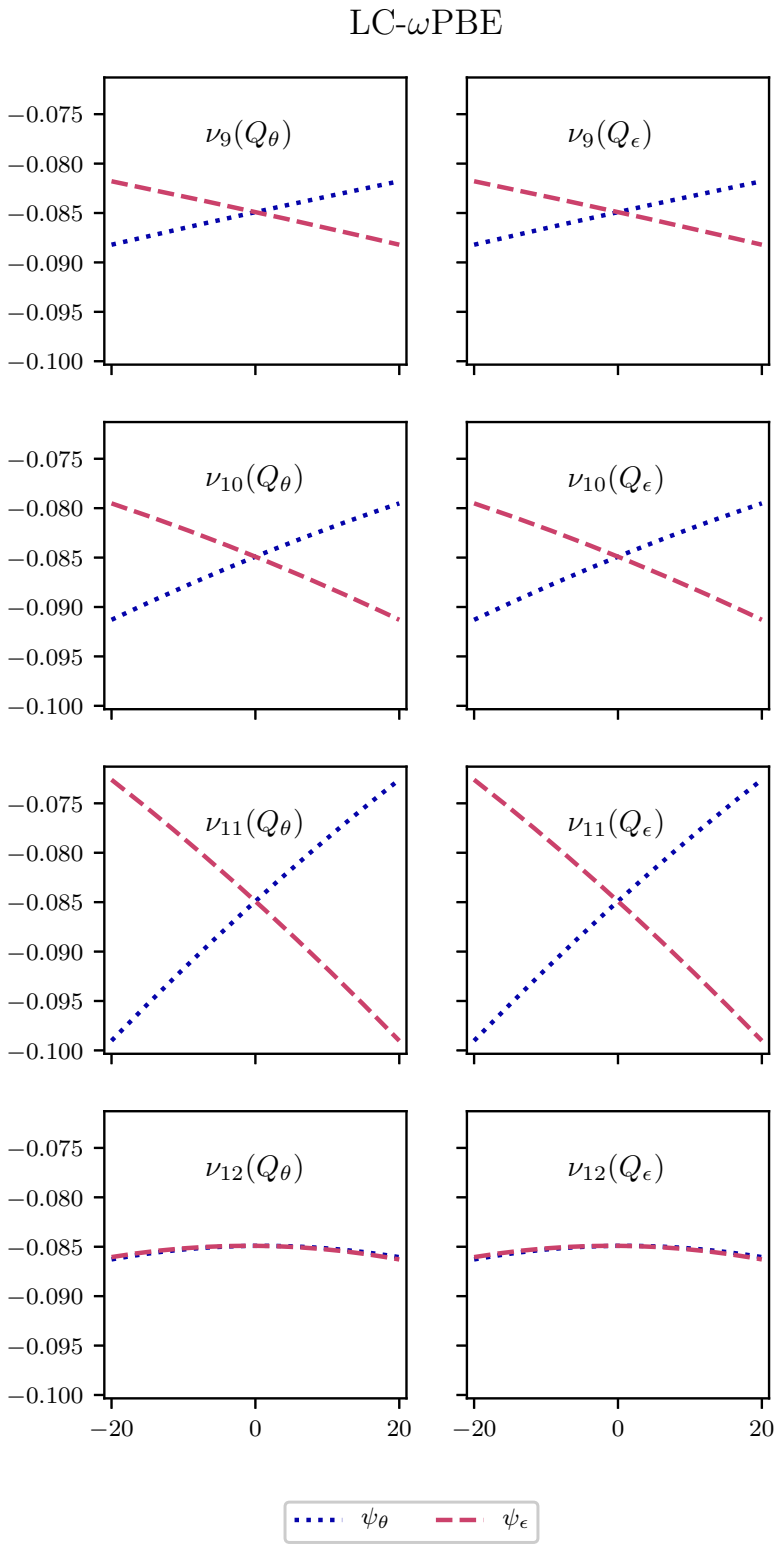

FIG. S11. LC-ωPBE energies of ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

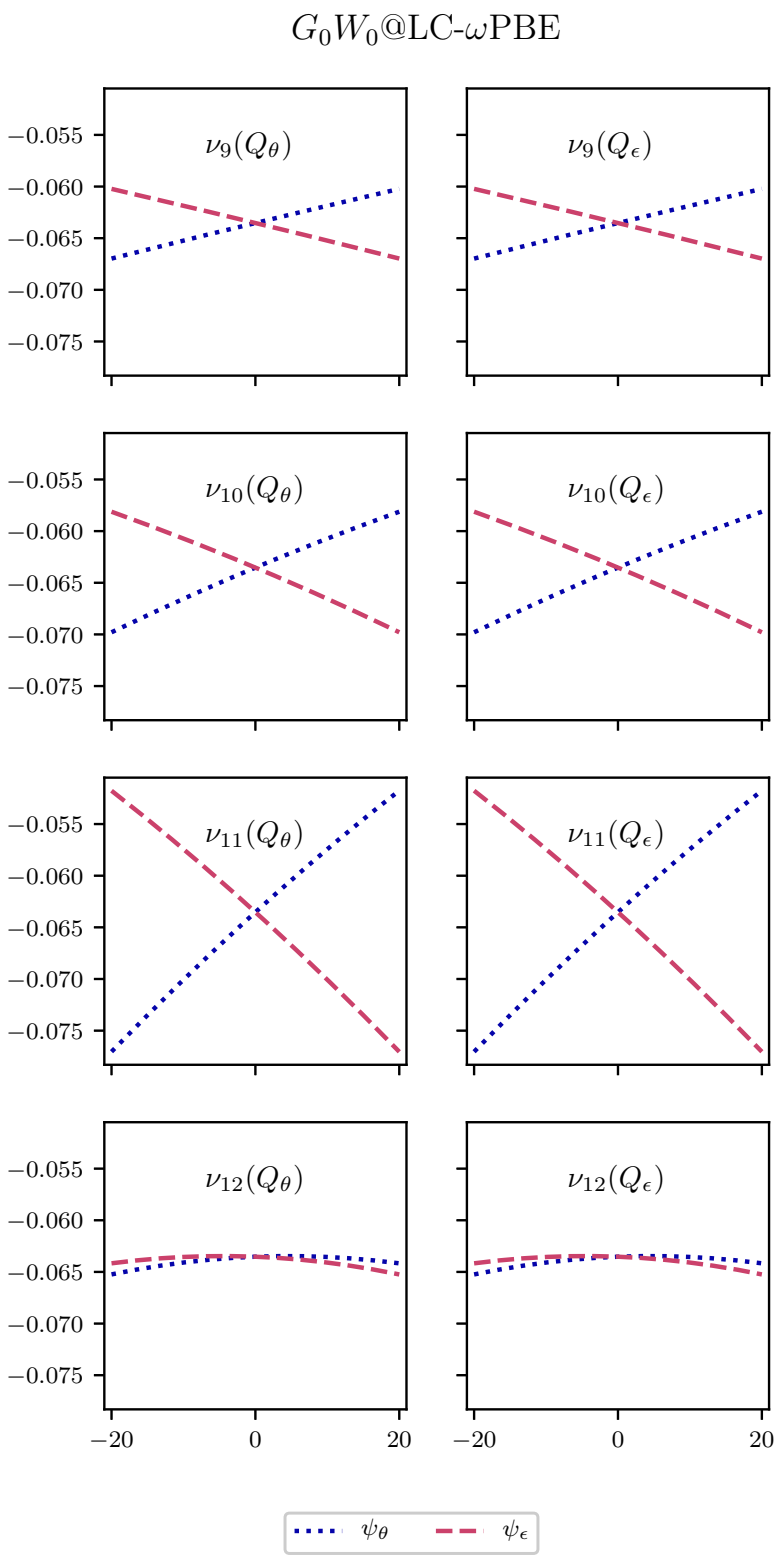

FIG. S12. G_0W_0@LC-ωPBE quasiparticle energies for ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

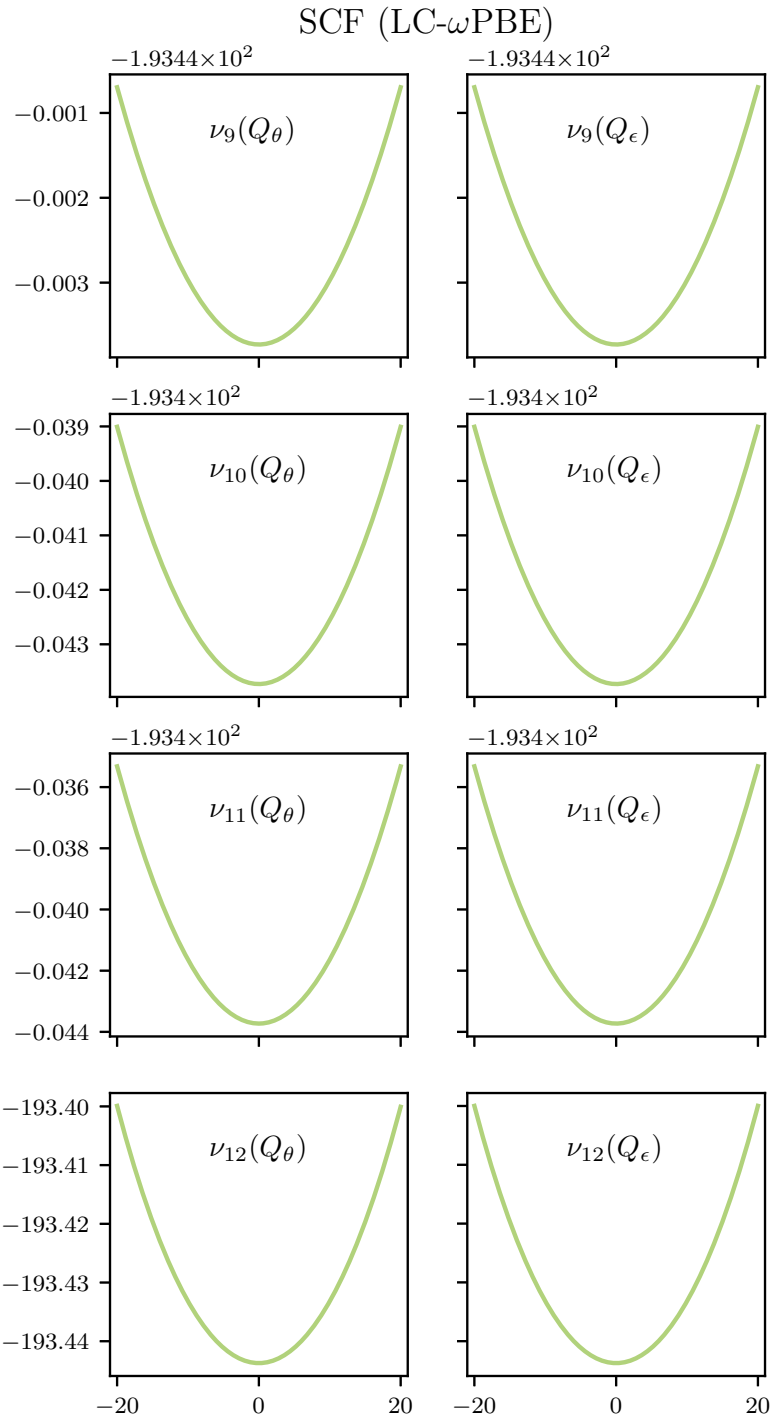

FIG. S13. LC-ωPBE SCF energies with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

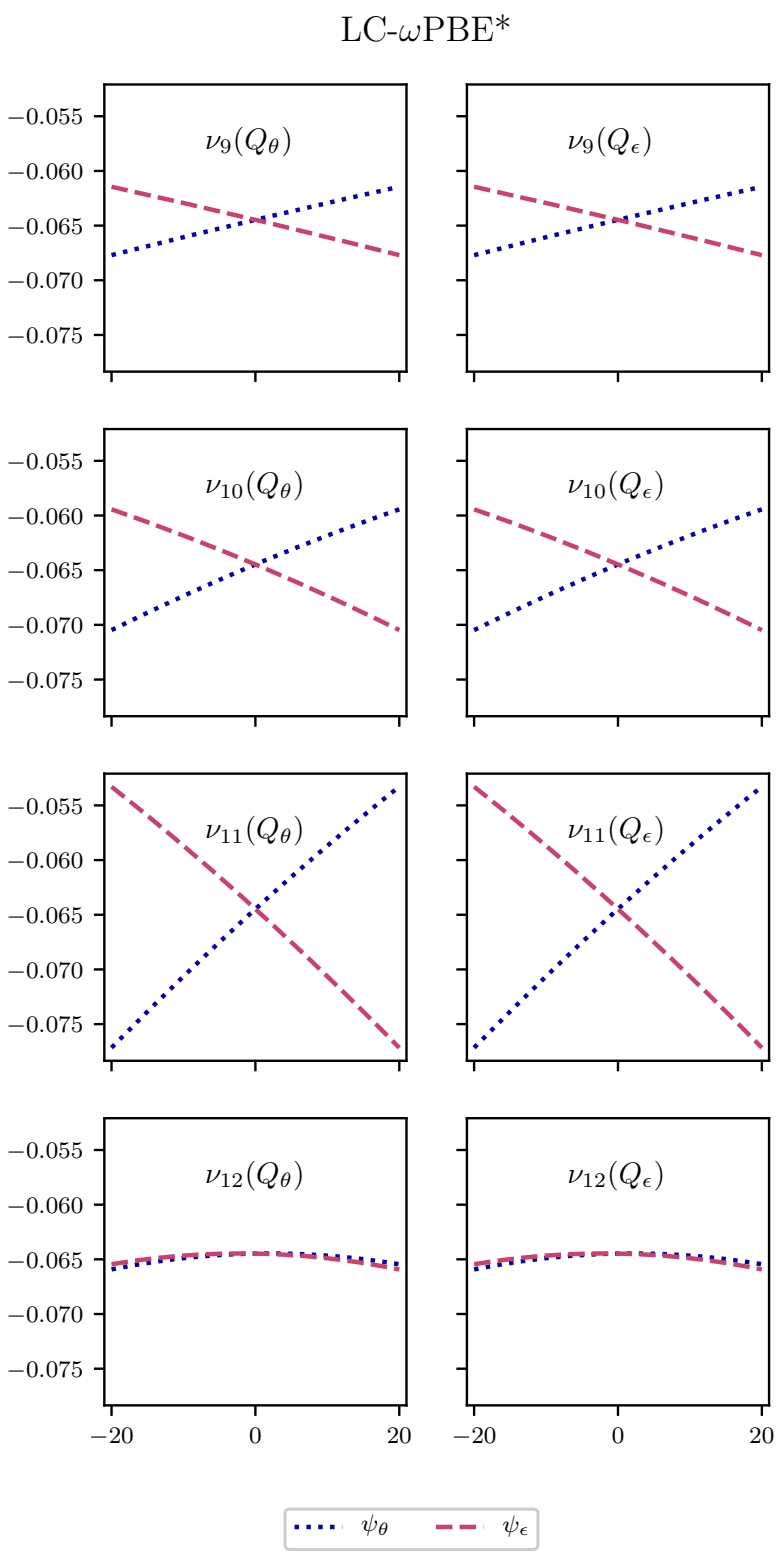

FIG. S14. LC-ωPBE* energies of ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

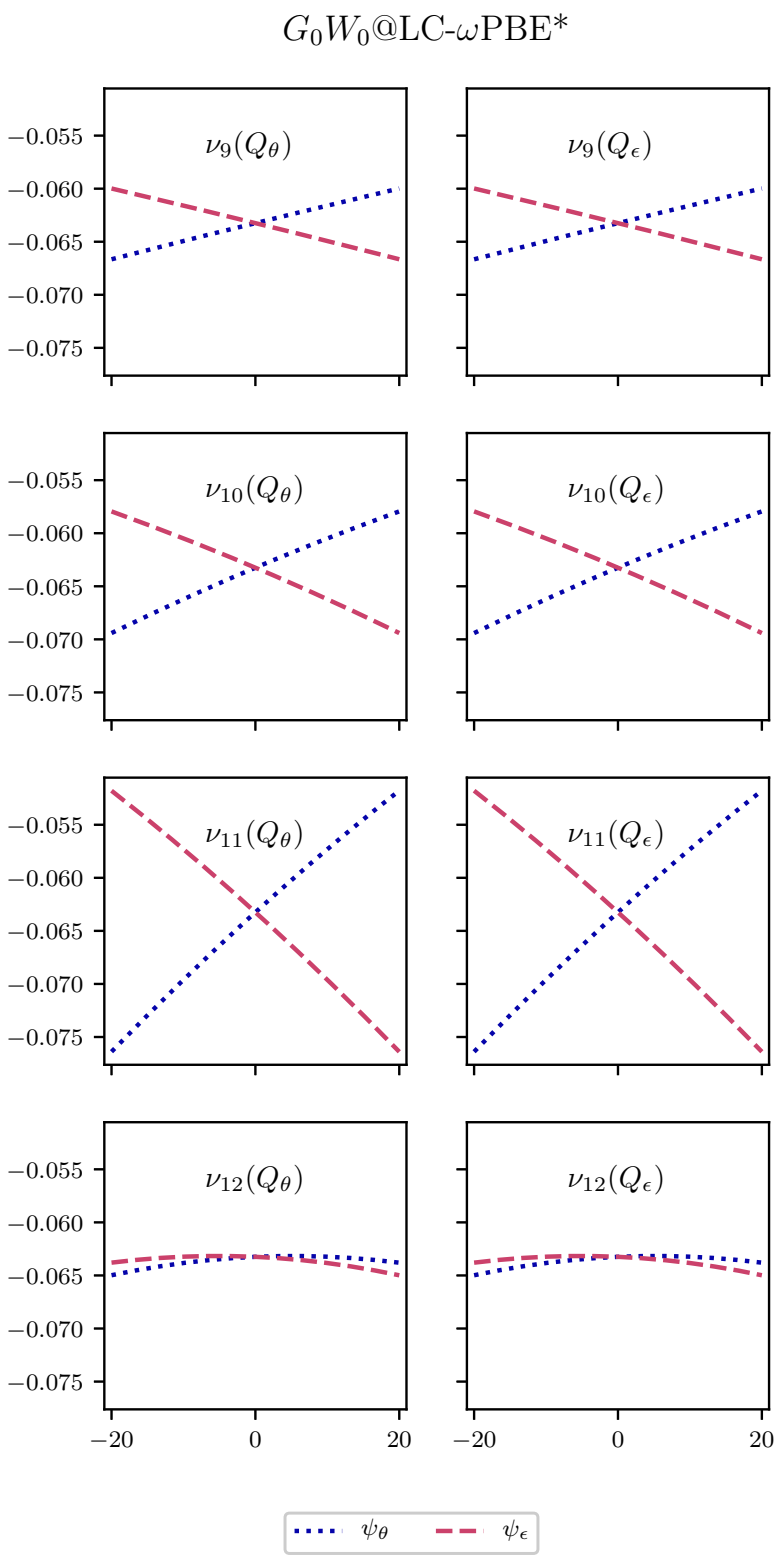

FIG. S15. G_0W_0@LC-ωPBE* quasiparticle energies for ψ_θ and ψ_ϵ with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

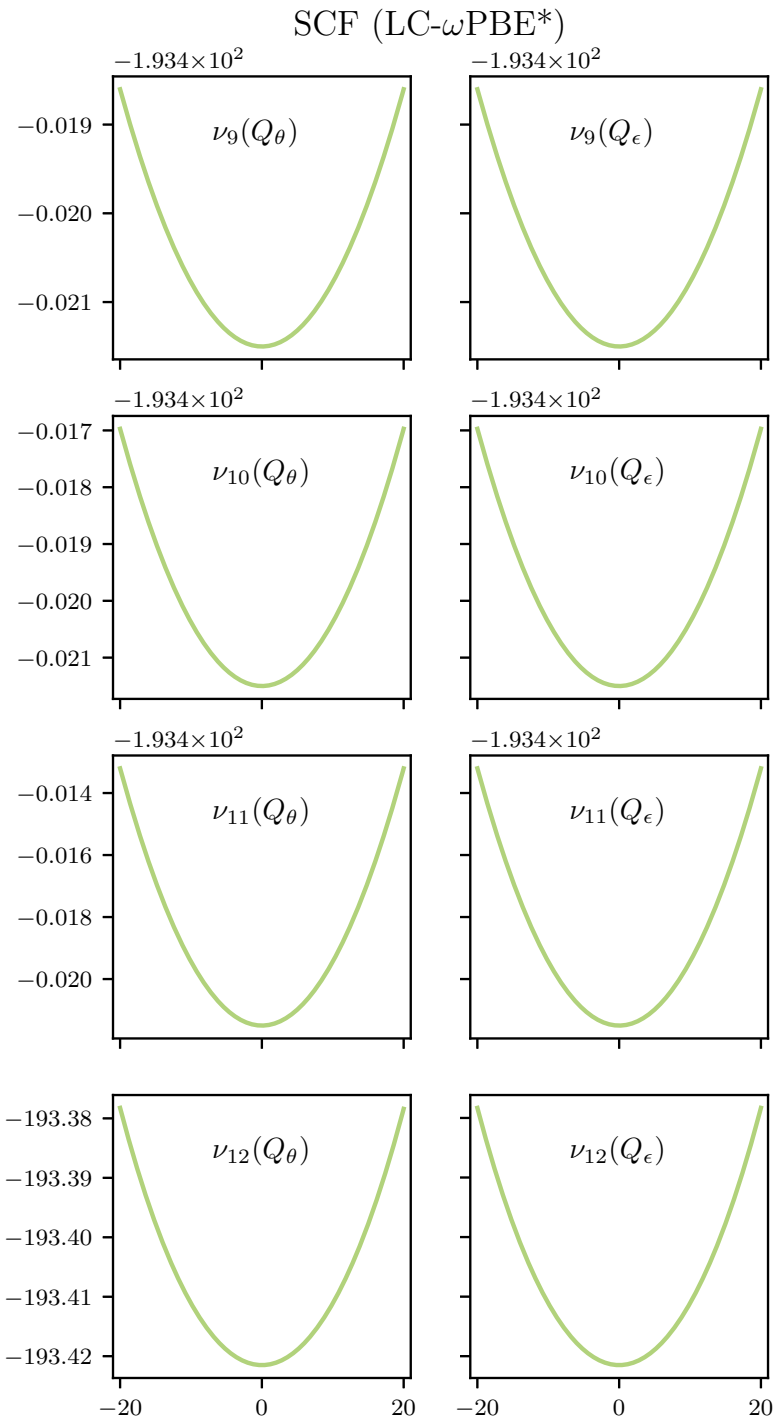

FIG. S16. LC-ωPBE* SCF energies with respect to distortions along the $e_2^{'}$ normal modes of the cyclopentadienyl anion.

S2. RESULTS

A. Basis set effect on linear vibronic coupling constants

On average, each single point cc-pVTZ (220 basis functions) calculation on the cyclopentadienyl anion took about 10-20 minutes to complete. A similar calculation using the cc-pVQZ basis (425 basis functions) took a few hours in comparison. Considering the small difference between the values of $V^{(1)}$ obtained using the two basis sets, we concluded that the computational cost of using the cc-pVQZ basis set to derive the vibronic coupling constants was not worth it. As a result, we used the cc-pVTZ basis in the *ab initio* calculations used in the derivation of vibronic coupling constants.

TABLE S13. Linear (orbital) vibronic coupling constant, $V^{(1)}$ (10^{-4} a.u.), for the ν_9 normal modes calculated using the energies of ψ_θ and ψ_θ and the cc-pVTZ and cc-pVQZ basis sets. The PBE0 functional was used here.

Mode	Orbital	cc-pVTZ	cc-pVQZ
$\nu_9(Q_\theta)$	ψ_θ	1.675	1.660
	ψ_ϵ	1.675	1.660
$\nu_9(Q_\epsilon)$	ψ_θ	1.676	1.661
	ψ_ϵ	1.676	1.661

B. Comparison of linear VCCs obtained using the degenerate HOMOs

From Tables S14 and S15, it can be seen that the values of the derived linear vibronic coupling constants obey the symmetry considerations disussed in the main text.

TABLE S14. Linear (orbital) vibronic coupling constant, $V^{(1)}$ (10^{-4} a.u.), for the $e_2^{'}$ normal modes calculated using the energies of ψ_θ and ψ_θ.

Mode	Orbital	HF	PBE	PBE0	LC-ωPBE	LC-ωPBE*
$\nu_9(Q_\theta)$	ψ_θ	1.897	1.619	1.675	1.605	1.563
	ψ_ϵ	1.897	1.619	1.675	1.605	1.563
$\nu_9(Q_\epsilon)$	ψ_θ	1.898	1.620	1.676	1.606	1.564
	ψ_ϵ	1.898	1.620	1.676	1.606	1.564
$\nu_{10}(Q_\theta)$	ψ_θ	3.143	2.525	2.720	2.944	2.760
	ψ_ϵ	3.413	2.525	2.720	2.944	2.760
$\nu_{10}(Q_\epsilon)$	ψ_θ	3.144	2.526	2.721	2.945	2.760
	ψ_ϵ	3.144	2.526	2.721	2.945	2.760
$\nu_{11}(Q_\theta)$	ψ_θ	7.352	5.041	5.690	6.616	5.975
	ψ_ϵ	7.352	5.041	5.690	6.616	5.975
$\nu_{11}(Q_\epsilon)$	ψ_θ	7.352	5.041	5.689	6.615	5.974
	ψ_ϵ	7.352	5.041	5.689	6.615	5.974
$\nu_{12}(Q_\theta)$	ψ_θ	0.042	0.258	0.198	0.055	0.115
	ψ_ϵ	0.047	0.261	0.202	0.059	0.119
$\nu_{12}(Q_\epsilon)$	ψ_θ	0.044	0.259	0.200	0.057	0.117
	ψ_ϵ	0.044	0.259	0.200	0.057	0.117

TABLE S15. Linear (orbital) vibronic coupling constant, $V^{(1)}$ (10^{-4} a.u.), for the $e_2^{'}$ normal modes calculated using the gradients of the G_0W_0 quasiparticle energies for ψ_θ and ψ_θ.

Mode	Orbital	G_0W_0@HF	G_0W_0@PBE	G_0W_0@PBE0	G_0W_0@LC-ωPBE	G_0W_0@LC-ωPBE*
$\nu_9(Q_\theta)$	ψ_θ	1.753	1.589	1.649	1.687	1.668
	ψ_ϵ	1.753	1.589	1.649	1.687	1.668
$\nu_9(Q_\epsilon)$	ψ_θ	1.752	1.590	1.650	1.688	1.668
	ψ_ϵ	1.752	1.590	1.650	1.688	1.668
$\nu_{10}(Q_\theta)$	ψ_θ	2.982	2.644	2.770	2.916	2.864
	ψ_ϵ	2.982	2.644	2.770	2.916	2.864
$\nu_{10}(Q_\epsilon)$	ψ_θ	2.983	2.644	2.770	2.917	2.865
	ψ_ϵ	2.983	2.644	2.770	2.917	2.865
$\nu_{11}(Q_\theta)$	ψ_θ	6.688	5.513	5.890	6.326	6.156
	ψ_ϵ	6.688	5.513	5.890	6.326	6.156
$\nu_{11}(Q_\epsilon)$	ψ_θ	6.687	5.513	5.890	6.325	6.155
	ψ_ϵ	6.687	5.513	5.890	6.325	6.155
$\nu_{12}(Q_\theta)$	ψ_θ	0.140	0.330	0.290	0.269	0.297
	ψ_ϵ	0.136	0.332	0.292	0.272	0.300
$\nu_{12}(Q_\epsilon)$	ψ_θ	0.138	0.331	0.291	0.270	0.298
	ψ_ϵ	0.138	0.331	0.291	0.270	0.298

C. Higher order vibronic coupling constants

TABLE S16. Higher order vibronic coupling constants derived using HF. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.8965	2.4576				10.913	227.12
	3	1.8967	2.4576	-1.2112			10.912	227.15
	4	1.8967	2.4547	-1.2112	0.2972	2.0336	10.907	227.23
$\nu_9(\epsilon)$	2	1.8973	2.4576				10.918	227.31
	3	1.8975	2.4576	-1.2378			10.917	227.34
	4	1.8975	2.4547	-1.2378		2.0293	10.912	227.43
$\nu_{10}(\theta)$	2	3.1445	3.8559				-11.533	-397.96
	3	3.1431	3.8559	6.9397			-11.536	-397.80
	4	3.1431	3.8303	6.9397	0.4469	17.7186	-11.496	-398.41
$\nu_{10}(\epsilon)$	2	3.1454	3.8558				-11.537	-398.20
	3	3.1440	3.8558	6.8264			-11.540	-398.05
	4	3.1440	3.8302	6.8264		17.7311	-11.500	-398.66
$\nu_{11}(\theta)$	2	7.3426	6.1406				-16.910	-1362.58
	3	7.3524	6.1406	-48.4434			-16.854	-1361.94
	4	7.3524	6.1017	-48.4434	19.7832	26.9524	-16.602	-1355.74
$\nu_{11}(\epsilon)$	2	7.3421	6.1408				-16.909	-1362.33
	3	7.3518	6.1408	-48.3442			-16.852	-1361.69
	4	7.3518	6.1019	-48.3442		26.9613	-16.623	-1356.47

TABLE S17. Higher order vibronic coupling constants derived using PBE. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.6196	1.9544				-11.719	-208.29
	3	1.6191	1.9544	2.3397			-11.722	-208.23
	4	1.6191	1.9522	2.3397	0.3137	1.5160	-11.714	-208.28
$\nu_9(\epsilon)$	2	1.6202	1.9544				-11.724	-208.45
	3	1.6198	1.9544	2.3232			-11.726	-208.40
	4	1.6198	1.9523	2.3232		1.5121	-11.719	-208.45
$\nu_{10}(\theta)$	2	2.5260	3.1145				-11.470	-317.94
	3	2.5252	3.1145	4.0009			-11.472	-317.85
	4	2.5252	3.0886	4.0009	-0.0311	17.9679	-11.424	-318.49
$\nu_{10}(\epsilon)$	2	2.5265	3.1146				-11.472	-318.07
	3	2.5257	3.1146	3.9322			-11.474	-317.98
	4	2.5257	3.0886	3.9322		17.9797	-11.426	-318.62
$\nu_{11}(\theta)$	2	5.0416	5.7159				-12.474	-690.12
	3	5.0414	5.7159	1.0534			-12.474	-690.09
	4	5.0414	5.6826	1.0534	14.4721	23.0577	-12.410	-690.29
$\nu_{11}(\epsilon)$	2	5.0411	5.7158				-12.473	-689.99
	3	5.0409	5.7158	1.1818			-12.473	-689.96
	4	5.0409	5.6826	1.1818		23.0674	-12.417	-690.38

TABLE S18. Higher order vibronic coupling constants derived using LC-ωPBE. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, $\rho_{min.}$ refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.6053	2.1437				-10.591	-186.57
	3	1.6052	2.1437	0.7925			-10.591	-186.55
	4	1.6052	2.1410	0.7925	0.3434	1.8773	-10.587	-186.63
$\nu_9(\epsilon)$	2	1.6061	2.1436				-10.596	-186.75
	3	1.6059	2.1436	0.7750			-10.597	-186.74
	4	1.6059	2.1410	0.7750		1.8088	-10.593	-186.81
$\nu_{10}(\theta)$	2	2.9449	3.3351				-12.488	-403.55
	3	2.9441	3.3351	4.0714			-12.491	-403.47
	4	2.9441	3.3082	4.0714	0.0173	18.6538	-12.413	-403.81
$\nu_{10}(\epsilon)$	2	2.9457	3.3354				-12.490	-403.75
	3	2.9449	3.3354	3.9827			-12.493	-403.67
	4	2.9449	3.3086	3.9827		18.5636	-12.415	-404.01
$\nu_{11}(\theta)$	2	6.6088	5.9391				-15.737	-1141.30
	3	6.6159	5.9391	-35.0689			-15.702	-1141.25
	4	6.6159	5.9034	-35.0689	15.8021	24.6877	-15.521	-1137.90
$\nu_{11}(\epsilon)$	2	6.6083	5.9394				-15.735	-1141.05
	3	6.6153	5.9394	-35.0123			-15.700	-1141.00
	4	6.6153	5.9045	-35.0123		24.1490	-15.538	-1138.31

TABLE S19. Higher order vibronic coupling constants derived using LC-ωPBE*. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.5631	2.0489				-10.789	-185.07
	3	1.5628	2.0489	1.5079			-10.790	-185.03
	4	1.5628	2.0464	1.5079	0.3415	1.7533	-10.785	-185.10
$\nu_9(\epsilon)$	2	1.5638	2.0490				-10.794	-185.23
	3	1.5635	2.0490	1.4883			-10.795	-185.20
	4	1.5635	2.0464	1.4883		1.7497	-10.790	-185.27
$\nu_{10}(\theta)$	2	2.7604	3.1982				-12.206	-369.75
	3	2.7596	3.1982	3.8163			-12.209	-369.67
	4	2.7596	3.1716	3.8163	-0.0268	18.4407	-12.138	-370.11
$\nu_{10}(\epsilon)$	2	2.7611	3.1982				-12.209	-369.94
	3	2.7604	3.1982	3.7388			-12.212	-369.86
	4	2.7604	3.1716	3.7388		18.4525	-12.141	-370.30
$\nu_{11}(\theta)$	2	5.9709	5.8608				-14.408	-944.05
	3	5.9747	5.8608	-18.6329			-14.394	-944.23
	4	5.9747	5.8266	-18.6329	14.7355	23.7436	-14.269	-942.81
$\nu_{11}(\epsilon)$	2	5.9704	5.8608				-14.407	-943.89
	3	5.9742	5.8608	-18.5522			-14.392	-944.06
	4	5.9742	5.8265	-18.5522		23.7538	-14.280	-943.04

TABLE S20. Higher order vibronic coupling constants derived using G_0W_0@HF. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.7516	2.4576				-10.080	-193.75
	3	1.7518	2.4576	-0.6261			-10.079	-193.77
	4	1.7518	2.4547	-0.6261	0.3804	2.0336	-10.077	-193.86
$\nu_9(\epsilon)$	2	1.7524	2.4576				-10.084	-193.92
	3	1.7525	2.4576	-0.6543			-10.084	-193.94
	4	1.7525	2.4547	-0.6543		2.0293	-10.082	-194.03
$\nu_{10}(\theta)$	2	2.9834	3.8559				-10.942	-358.22
	3	2.9820	3.8559	6.6991			-10.944	-358.06
	4	2.9820	3.8303	6.6991	-0.2174	17.7186	-10.917	-358.80
$\nu_{10}(\epsilon)$	2	2.9842	3.8558				-10.945	-358.43
	3	2.9829	3.8558	6.6222			-10.948	-358.27
	4	2.9829	3.8302	6.6222		17.7311	-10.920	-359.01
$\nu_{11}(\theta)$	2	6.6800	6.1406				-15.384	-1127.75
	3	6.6879	6.1406	-39.0541			-15.350	-1127.82
	4	6.6879	6.1017	-39.0541	33.5285	26.9524	-15.160	-1124.23
$\nu_{11}(\epsilon)$	2	6.6795	6.1408				-15.383	-1127.53
	3	6.6874	6.1408	-39.0776			-15.348	-1127.59
	4	6.6874	6.1019	-39.0776		26.9613	-15.189	-1125.16

TABLE S21. Higher order vibronic coupling constants derived using G_0W_0@PBE. $V_\gamma^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.5892	1.9544				-11.500	-200.55
	3	1.5893	1.9544	-0.1481			-11.499	-200.55
	4	1.5893	1.9522	-0.1481	0.2994	1.5160	-11.492	-200.60
$\nu_9(\epsilon)$	2	1.5899	1.9544				-11.504	-200.72
	3	1.5899	1.9544	-0.1716			-11.504	-200.72
	4	1.5899	1.9523	-0.1716		1.5121	-11.497	-200.77
$\nu_{10}(\theta)$	2	2.6449	3.1145				-12.010	-348.59
	3	2.6437	3.1145	6.3598			-12.015	-348.45
	4	2.6437	3.0886	6.3598	-0.6177	17.9679	-11.950	-348.95
$\nu_{10}(\epsilon)$	2	2.6456	3.1146				-12.013	-348.76
	3	2.6443	3.1146	6.2993			-12.017	-348.62
	4	2.6443	3.0886	6.2993		17.9797	-11.952	-349.11
$\nu_{11}(\theta)$	2	5.5108	5.7159				-13.635	-824.55
	3	5.5134	5.7159	-12.5814			-13.627	-824.73
	4	5.5134	5.6826	-12.5814	24.6354	23.0577	-13.522	-823.88
$\nu_{11}(\epsilon)$	2	5.5104	5.7158				-13.634	-824.44
	3	5.5128	5.7158	-11.9219			-13.626	-824.61
	4	5.5128	5.6826	-11.9219		23.0674	-13.538	-824.29

TABLE S22. Higher order vibronic coupling constants derived using G_0W_0@PBE0. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.6488	2.0953				-11.128	-201.34
	3	1.6488	2.0953	-0.1337			-11.128	-201.35
	4	1.6488	2.0930	-0.1337	0.3168	1.6215	-11.122	-201.41
$\nu_9(\epsilon)$	2	1.6495	2.0953				-11.133	-201.52
	3	1.6495	2.0953	-0.1579			-11.133	-201.52
	4	1.6495	2.0930	-0.1579		1.6175	-11.127	-201.58
$\nu_{10}(\theta)$	2	2.7709	3.3298				-11.769	-357.86
	3	2.7696	3.3298	6.5871			-11.773	-357.71
	4	2.7696	3.3040	6.5871	-0.3095	17.8736	-11.720	-358.27
$\nu_{10}(\epsilon)$	2	2.7717	3.3298				-11.772	-358.04
	3	2.7703	3.3298	6.5262			-11.776	-357.89
	4	2.7703	3.3040	6.5262		17.8856	-11.722	-358.45
$\nu_{11}(\theta)$	2	5.8873	5.8738				-14.175	-915.76
	3	5.8902	5.8738	-14.6038			-14.164	-915.92
	4	5.8902	5.8398	-14.6038	22.6325	23.5324	-14.043	-914.56
$\nu_{11}(\epsilon)$	2	5.8868	5.8738				-14.173	-915.60
	3	5.8897	5.8738	-14.3133			-14.163	-915.76
	4	5.8897	5.8398	-14.3133		23.5420	-14.059	-914.97

TABLE S23. Higher order vibronic coupling constants derived using G_0W_0@LC-ωPBE. $V_\gamma^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.6868	2.1437				-11.128	-205.98
	3	1.6868	2.1437	-0.2425			-11.128	-205.98
	4	1.6868	2.1410	-0.2425	0.3108	1.8773	-11.121	-206.06
$\nu_9(\epsilon)$	2	1.6875	2.1436				-11.133	-206.17
	3	1.6876	2.1436	-0.2603			-11.133	-206.18
	4	1.6876	2.1410	-0.2603		1.8088	-11.127	-206.25
$\nu_{10}(\theta)$	2	2.9173	3.3351				-12.371	-396.04
	3	2.9162	3.3351	5.4533			-12.375	-395.93
	4	2.9162	3.3082	5.4533	-0.1340	18.6538	-12.301	-396.32
$\nu_{10}(\epsilon)$	2	2.9181	3.3354				-12.373	-396.22
	3	2.9170	3.3354	5.3793			-12.377	-396.11
	4	2.9170	3.3086	5.3793		18.5636	-12.303	-396.49
$\nu_{11}(\theta)$	2	6.3213	5.9391				-15.052	-1044.17
	3	6.3256	5.9391	-21.2429			-15.034	-1044.26
	4	6.3256	5.9034	-21.2429	22.6162	24.6877	-14.875	-1041.73
$\nu_{11}(\epsilon)$	2	6.3208	5.9394				-15.050	-1043.94
	3	6.3251	5.9394	-21.1172			-15.032	-1044.03
	4	6.3251	5.9045	-21.1172		24.1490	-14.896	-1042.26

TABLE S24. Higher order vibronic coupling constants derived using G_0W_0@LC-ωPBE*. $V_{\gamma}^{(i)}$ refers to the i^{th} order vibronic coupling constant with respect to the symmetry representation γ, ρ_{min} refers to the molecular structure at which the energy of the system is at a minima with respect to the distortion along a $e_2^{'}$ normal mode, and $E_{JT}^{(i)}$ refers to the JT stabilisation energy, where i is the order of the model Hamiltonian used. All values are in a.u. except for the stabilisation energies, which is given in cm^{-1}

Mode	Order	$V_{e_2^{'}}^{(1)} \times 10^{-4}$	$V_{a_1^{'}}^{(2)} \times 10^{-5}$	$V_{e_2^{'}}^{(3)} \times 10^{-9}$	$V_{e_2^{'}}^{(4)} \times 10^{-10}$	$V_{a_1^{'}}^{(4)} \times 10^{-9}$	$\rho_{min.}$	$E_{JT}^{(i)}$
$\nu_9(\theta)$	2	1.6675	2.0489				-11.509	-210.61
	3	1.6676	2.0489	-0.2102			-11.509	-210.61
	4	1.6676	2.0464	-0.2102	0.2948	1.7533	-11.501	-210.67
$\nu_9(\epsilon)$	2	1.6682	2.0490				-11.514	-210.79
	3	1.6683	2.0490	-0.2345			-11.514	-210.80
	4	1.6683	2.0464	-0.2345		1.7497	-11.507	-210.86
$\nu_{10}(\theta)$	2	2.8653	3.1982				-12.670	-398.38
	3	2.8642	3.1982	5.5934			-12.675	-398.28
	4	2.8642	3.1716	5.5934	-0.0960	18.4407	-12.588	-398.54
$\nu_{10}(\epsilon)$	2	2.8660	3.1982				-12.673	-398.59
	3	2.8649	3.1982	5.5256			-12.678	-398.48
	4	2.8649	3.1716	5.5256		18.4525	-12.591	-398.74
$\nu_{11}(\theta)$	2	6.1523	5.8608				-14.845	-1002.27
	3	6.1560	5.8608	-18.5747			-14.830	-1002.38
	4	6.1560	5.8266	-18.5747	19.0595	23.7436	-14.685	-1000.30
$\nu_{11}(\epsilon)$	2	6.1518	5.8608				-14.844	-1002.10
	3	6.1555	5.8608	-18.4142			-14.829	-1002.21
	4	6.1555	5.8265	-18.4142		23.7538	-14.701	-1000.71