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

Can one use the electronic absorption spectra of metalloporphyrins to benchmark electronic structure methods? A case study on the cobalt porphyrin

Jhonathan Rosa de Souza[1], Matheus Morato F. de Moraes[2], Yuri Alexandre Aoto*[2],

Paula Homem-de-Mello*[1]

[1] Centro de Ciências Naturais e Humanas (CCNH), Universidade Federal do ABC (UFABC), Av. dos Estados, 5001, Santo André, SP, Brazil, 09210-580

[2] Centro de Matemática, Computação e Cognição (CMCC), Universidade Federal do ABC (UFABC), Av. dos Estados, 5001, Santo André, SP, Brazil, 09210-580

*Correspondence to Yuri Alexandre Aoto (E-mail: yuri.aoto@ufabc.edu.br); Paula Homem-de-Mello (E-mail: paula.mello@ufabc.edu.br)

SUPPLEMENTARY INFORMATION

1. Reference data

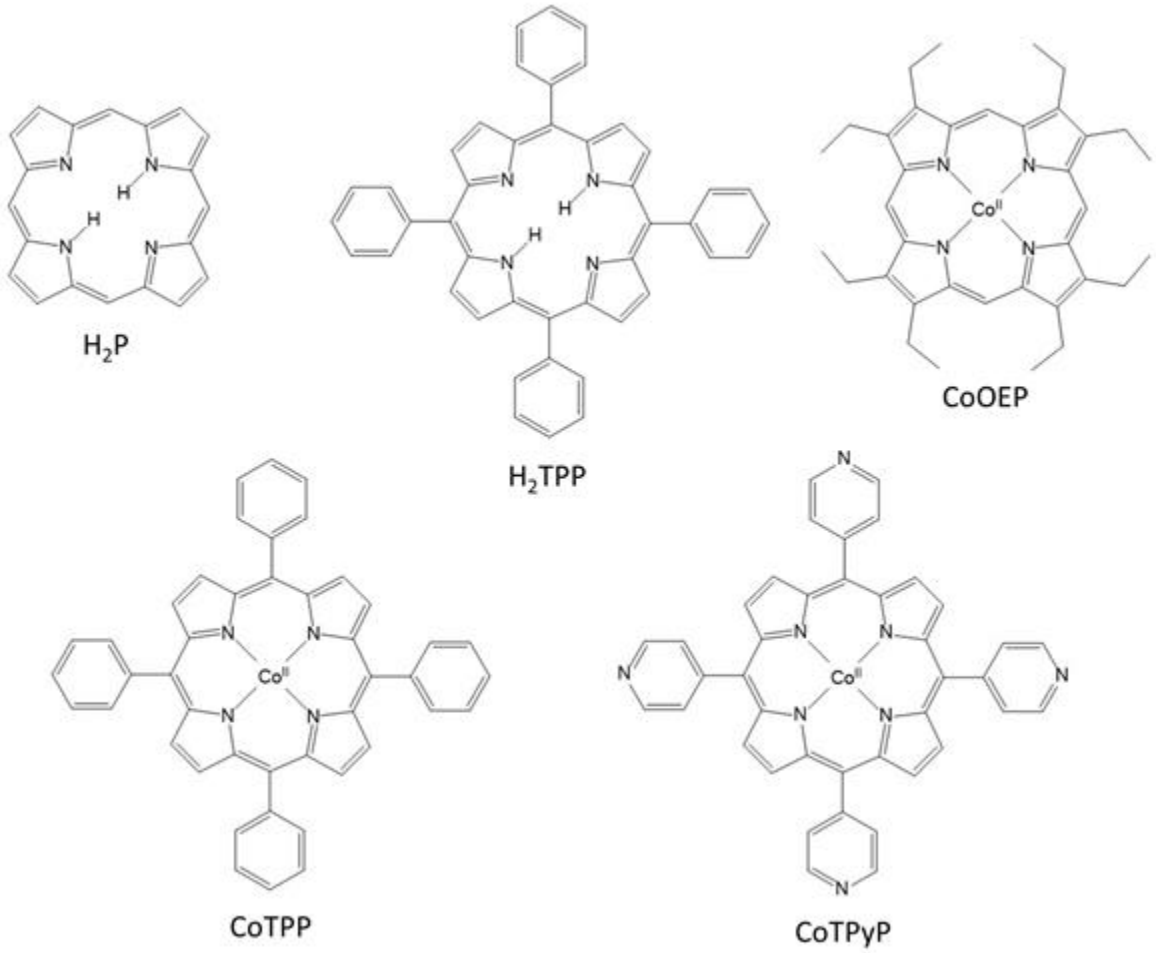

Figure SI1. Molecular structure of the derivatives used as comparison.

Table SI1. Experimental spectrophotometry data for Q-band of H_2P, H_2TPP, CoTPP and CoTPyP

Molecule	Solvent	T (°C)	Q(0-0) (nm)	Q(1-0) (nm)	ε ($cm^{-1}M^{-1}$)	Ref.
H_2P	Vapor	393	627.5 (x)	575.0 (x)	-	*a*
	Vapor	393	511.5 (y)	483.5 (y)	-	
	Benzene	25	617.3 (x)	564.0 (x)	-	
	Benzene	25	520.8 (y)	490.3 (y)	-	
	Ethanol	-180	613.4 (x)	560.6 (x)	-	
	Ethanol	-180	519.0 (y)	487.5 (y)	-	
	Dichloro-Methane	25	613.5 (x)	560.0 (x)	-	
	Dichloro-Methane	25	518.0 (y)	488.0 (y)	-	
H_2TPP	Vapor	448	664.0 (x)	602.5 (x)	-	*b*
	Vapor	448	546.0 (y)	510.5 (y)	-	
	Benzene	25	650.0 (x)	590.5 (x)	-	
	Benzene	25	548.0 (y)	512.0 (y)	-	
	Oil	304	658.0 (x)	600.0 (x)	-	
	Oil	304	552.5 (y)	517.0 (y)	-	
	Oil	30	649.5 (x)	591.0 (x)	-	
	Oil	30	548.5 (y)	514.5 (y)	-	
	DMOE	25	646.5 (x)	590.0 (x)	-	
	DMOE	25	545.5 (y)	512.0 (y)	-	
	Dichloro-Methane	25	646.5 (x)	590.0 (x)	-	
	Dichloro-Methane	25	548.5 (y)	514.0 (y)	-	
H_2TPP	Dichloro-Methane	-	620	585	-	*f*
	Dichloro-Methane		538	514	-	

Table SI1: continuation

Molecule	Solvent	T (°C)	Q(0-0) (nm)	Q(1-0) (nm)	ε ($cm^{-1}M^{-1}$)	Ref.
CoTPP	Vapor	469	-	533	-	*a*
	Benzene	25	-	530	-	
	Dichloro-Methane	25	-	528	-	
CoTPP	Benzene	45	529		0.000170	*b*
	Toluene	45	529		0.000180	
	Dichloro-Methane	23	528		0.000160	*c*
CoTPP	Pyridine	-	533		0.000100	*d*
	PhCN	-	531		0.000150	
	Dichloro-Methane	-	528		0.000130	
CoTPP	PhCN	22	530		0.000126	*e*
CoTPP	Dichloro-Methane	-	528		-	*f*
CoTPyP	Chloroform/Methanol	-	563[#]	531*	-	*g*
	Chloroform/Methanol	-	553[#]	522[#]	-	

a Edwards *et. al, J. Mol. Spec.* **38** (1971) 16; https://doi.org/10.1016/0022-2852(71)90090-7
b Mu *et. al*, *Electroanalysis* **1** (1989) 113; https://doi.org/10.1002/elan.1140010205
c Kadish *et. al*, *Inorg. Chem.* **27** (1987) 4161; https://doi.org/10.1021/ic00272a006
d Ke *et. al*, *Inorg. Chem.* **57** (2018) 1490; https://doi.org/10.1021/acs.inorgchem.7b02856
e D'Souza *et. al*, *Inorg. Chem.* **32** (1993) 4042; https://doi.org/10.1021/ic00071a012
f Pamin *et. al*, *ChemSusChem* **12** (2018) 684; https://doi.org/10.1002/cssc.201802198
g Lopes *et. al*, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **215** (2019) 327; https://doi.org/10.1016/j.saa.2019.02.024
* Maximum absorption Q-band peak
[#] Values obtained by deconvolution method using Voigt functions

Table SI2. Experimental spectrophotometry data for B-band (Soret band) of H_2P, H_2TPP, CoTPP and CoTPyP

Molecules	Solvent	T (°C)	B (nm)	ε ($cm^{-1}M^{-1}$)	Ref.
H_2P	Vapor	322	372.5	-	*a*
	Benzene	25	396.5	-	
	Ethanol	-180	390.6	-	
	Dichloro-Methane	25	393.5	-	
H_2TPP	Vapor	395	402.5	-	*b*
	Benzene	25	418.5	-	
	Oil	294	419.0	-	
	Oil	32	418.0	-	
	DMOE	25	415.0	-	
	Dichloro-Methane	25	416.0	-	
H_2TPP	Dichloro-Methane	-	417.0	-	*f*
CoTTP	Vapor	393	398.5	-	*a*
	Benzene	25	414.6	-	
	Dichloro-Methane	25	404.0	-	
CoTTP	Benzene	45	412.0	0.002900	*b*
	Toluene	45	412.0	0.002600	
	Dichloro-Methane	23	410.0	0.002900	*c*
CoTPP	Pyridine	-	409.0	0.001800	*d*
	PhCN	-	417.0	0.002360	
	Dichloro-Methane	-	411.0	0.002100	
CoTPP	PhCN	22	416.8	0.001785	*e*
CoTPP	Dichloro-Methane	-	410.0	-	*f*
CoTPyP	Chloroform/Methanol	-	411.0	-	*g*

a Edwards *et. al,* J Mol Spec. **38** (1971) 16; https://doi.org/10.1016/0022-2852(71)90090-7
b Mu *et. al*, *Electroanalysis* **1** (1989) 113; https://doi.org/10.1002/elan.1140010205
c Kadish *et. al*, *Inorg. Chem.* **27** (1987) 4161; https://doi.org/10.1021/ic00272a006

d Ke *et. al*, *Inorg. Chem.* **57** (2018) 1490; https://doi.org/10.1021/acs.inorgchem.7b02856
e D'Souza *et. al*, *Inorg. Chem.* **32** (1993) 4042; https://doi.org/10.1021/ic00071a012
f Pamin *et. al*, *ChemSusChem* **12** (2018) 684; https://doi.org/10.1002/cssc.201802198
g Lopes *et. al*, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **215** (2019) 327; https://doi.org/10.1016/j.saa.2019.02.024

2. Ground state geometries and properties

CoP optimized geometries, both at doublet and quartet state, are shown in Figure SI2. The obtained structures correspond to minima on potential energy surfaces since frequencies obtained are all real. The geometries at both states are planar, and the Co-N distances and the macrocycle in high-spin are slightly larger than in low-spin state.

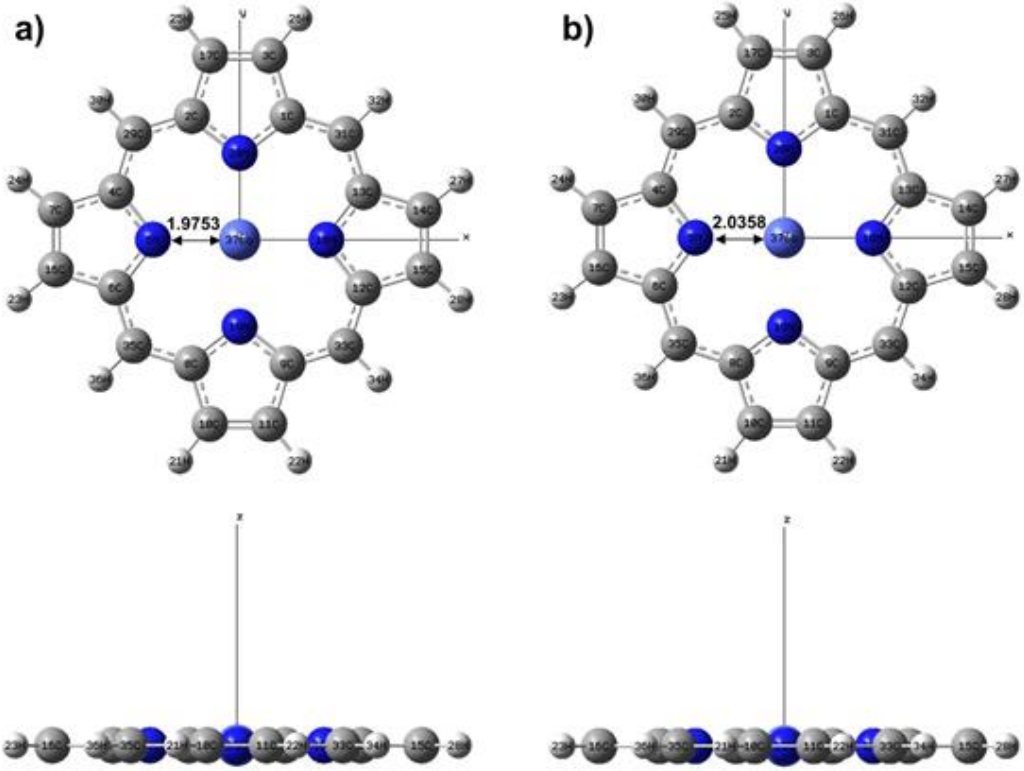

Figure SI2. Optimized Geometries of (a) doublet and (b) quartet states using TPSSh/D3BJ/def2-TZVP

Table SI3. Cartesian coordinates, in Angstrom, of optimized Geometries of (a) doublet and (b) quartet states using TPSSh/D3BJ/def2-TZVP

Doublet state				**Quartet state**			
C	1.091375	2.814753	0.000000	**C**	1.095491	2.851741	0.000000
C	-1.091375	2.814753	0.000000	**C**	-1.104278	2.858510	0.000000
C	0.678003	4.189989	0.000000	**C**	0.678737	4.230751	0.000000
C	-2.814753	1.091375	0.000000	**C**	-2.858510	1.104280	0.000000
N	-1.975350	0.000000	0.000000	**N**	-2.035742	0.005872	0.000000
C	-2.814753	-1.091374	0.000000	**C**	-2.851742	-1.095492	0.000000
C	-4.189989	0.678003	0.000000	**C**	-4.234736	0.682023	0.000000
C	-1.091374	-2.814753	0.000000	**C**	-1.095491	-2.851742	0.000000
C	1.091375	-2.814753	0.000000	**C**	1.104279	-2.858511	0.000000
C	-0.678003	-4.189989	0.000000	**C**	-0.678737	-4.230751	0.000000
C	0.678003	-4.189989	0.000000	**C**	0.682023	-4.234736	0.000000
C	2.814753	-1.091375	0.000000	**C**	2.858510	-1.104279	0.000000
C	2.814753	1.091374	0.000000	**C**	2.851741	1.095491	0.000000
C	4.189989	0.678002	0.000000	**C**	4.230751	0.678737	0.000000
C	4.189989	-0.678003	0.000000	**C**	4.234735	-0.682023	0.000000
C	-4.189989	-0.678003	0.000000	**C**	-4.230751	-0.678737	0.000000
C	-0.678003	4.189989	0.000000	**C**	-0.682023	4.234736	0.000000
N	1.975350	-0.000000	0.000000	**N**	2.035742	-0.005871	0.000000
N	0.000000	-1.975350	0.000000	**N**	0.005871	-2.035742	0.000000
N	-0.000000	1.975350	0.000000	**N**	-0.005871	2.035742	0.000000
H	-1.355418	-5.031172	0.000000	**H**	-1.348399	-5.078554	0.000000
H	1.355418	-5.031172	0.000000	**H**	1.347172	-5.085954	0.000000
H	-5.031171	-1.355418	0.000000	**H**	-5.078554	-1.348399	0.000000
H	-5.031172	1.355418	0.000000	**H**	-5.085954	1.347172	0.000000
H	-1.355418	5.031172	0.000000	**H**	-1.347172	5.085954	0.000000
H	1.355418	5.031172	0.000000	**H**	1.348400	5.078553	0.000000
H	5.031172	1.355418	0.000000	**H**	5.078553	1.348400	0.000000
H	5.031172	-1.355418	0.000000	**H**	5.085954	-1.347172	0.000000
C	-2.408724	2.408724	0.000000	**C**	-2.425134	2.425135	0.000000
H	-3.174560	3.174560	0.000000	**H**	-3.191575	3.191577	0.000000
C	2.408724	2.408724	0.000000	**C**	2.415980	2.415980	0.000000
H	3.174559	3.174559	0.000000	**H**	3.182443	3.182444	0.000000
C	2.408724	-2.408724	0.000000	**C**	2.425135	-2.425135	0.000000
H	3.174560	-3.174560	0.000000	**H**	3.191576	-3.191575	0.000000
C	-2.408724	-2.408724	0.000000	**C**	-2.415981	-2.415981	0.000000
H	-3.174559	-3.174559	0.000000	**H**	-3.182443	-3.182445	0.000000
Co	0.000000	0.000000	0.000000	**Co**	0.000000	0.000000	0.000000

Table SI4. Cobalt(II) to nitrogen average bond length for different porphyrinic systems

CoP					CoTPP				CoOEP
^2A_g *	$^4B_{1g}$ *	Ref. a	Ref. b	Ref. c	Ref. a	Ref. b	Ref. c	Ref. d	Ref. e
1.9753	2.0357	1.99	1.985	1.98	1.99	1.981	1.967	1.949	1.971

* This work, obtained with TPSSh/D3BJ/def2-TZVP

a B3LYP/LANL2DZ, from Roy *et. al*, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **190** (2018) 121; https://doi.org/10.1016/j.saa.2017.08.069

b PW/DNP, from Liu *et. al*, *J. Chem. Phys.*, **139** (2013) 204306; https://doi.org/10.1063/1.4832696

c VWN-B-P/triple-ζ STO, from Liao and Scheiner *J. Chem. Phys*. **117** (2002) 205; https://doi.org/10.1063/1.1480872

d X-ray diffraction crystals, from Madura and Scheidt *Inorg. Chem.* **15** (1976) 3182; https://doi.org/10.1021/ic50166a056

e X-ray diffraction crystals, from Scheidt and Turowska-Tyrk *Inorg. Chem.* **33** (1994) 1314; https://doi.org/10.1021/ic00085a017

Table SI5. Mulliken and electrostatic surface potential derived (ChelpG) charges obtained for Co(II) in doublet (A_g) and quartet (B_{1g}) states by DFT methods

State	BP86	OLYP	M06L	TPSSh	B3LYP	PBE0	M06	CAM-B3LYP	ωB97X
Mulliken									
^2A_g	-0.070	-0.238	0.265	0.108	0.072	0.067	-0.007	0.138	0.138
$^4B_{1g}$	-0.026	-0.172	0.304	0.168	0.109	0.111	-0.014	0.166	0.165
ChelpG									
^2A_g	0.346	0.399	0.418	0.411	0.403	0.446	0.371	0.432	0.462
$^4B_{1g}$	0.151	0.222	0.546	0.482	0.444	0.514	0.602	0.660	0.497

Table SI6. Spin contamination obtained with different functionals (ideal value: $\langle S^2 \rangle$ = 0.75)

	BP86	OLYP	M06L	TPSSh	B3LYP	PBE0	M06	CAM-B3LYP	wB97X
$\langle S^2 \rangle$	0.7614	0.7684	0.7673	0.7581	0.7564	0.7568	0.7606	0.7548	0.7546
Deviation (%)	1.52	2.46	2.31	1.07	0.86	0.91	1.42	0.64	0.61

3. Electronic absorption spectrum

Table SI7. Expected peaks in the UV-Vis region for CoTPP and CoP molecules in gas-phase

	CoTPP	CoP
Q(0-0) band	2.08 - 2.25 eV [(b)]	2.21 - 2.41 eV [(b)]
Q(1-0) band	2.23 - 2.43 eV [(a)]	2.38 - 2.61 eV [(b)]
B band	3.01 - 3.22 eV [(a)]	3.16 - 3.40 eV [(b)]
M band	6.20 eV (CoTTP and FBTPP) [(a)]	5.51 eV (free base) [(a)]
unnamed band 2	4.72 eV [(a)]	
unnamed band 1	1.61 eV [(a)]	

(a) experimental data from Edwards *et. al, J. Mol. Spec.* **38** (1971) 16; https://doi.org/10.1016/0022-2852(71)90090-7 and (b) estimated, see main text.

Table SI8 summarizes some literature assignment of the bands found in the UV-Vis spectrum of the free base porphyrin, obtained by several authors and methods. For a comparison of excitation energies see Table 2 of Angeli *et. Al* (https://doi.org/10.1007/s00214-006-0207-0). Whenever the excitations that contribute to the "x" and "y" bands are equivalent (e.g., Q and B bands), the contributions of each excitation are a rough average of x and y components, indicated by a "~". Since CoP is of point group C_{4h}, it is not important for us to distinguish between them. However, for some cases (e.g, N band of Serrano-Andrés *et. Al*, https://doi.org/10.1016/S0009-2614(98)00934-8) the assignment suggested by the authors does not consider x and y equivalently. For these cases two sets of contributions are given.

We adopted the notation of Parusel and Grimme for frontier orbitals. For orbitals where the transition originates (thus, occupied orbitals, in the left-hand side of "→" in the table below):

- b_{1u} is the HOMO of that symmetry;
- *n*b_{1u} is the HOMO-1 of that symmetry;
- *2n*b_{1u} is the HOMO-2 of that symmetry; and so on.

The final orbitals of the transition (thus, the unoccupied orbitals, in the right-hand side of "→") are always the Gouterman's LUMO orbitals (b_{2g}, b_{3g}).

Table SI8. Bands classification for a free-base porphyrin absorption spectrum as presented by Goutterman and selected wave function calculations

	Gouterman (1960s) 4-orbital model[a]	**Tokita et al.[b]** **SAC-CI**	**Serrano-Andrés et al.[c]** **CASSCF (16,14) ANO-S C,N [3s2p1d]/H[2s]** **Orbitals in the active space: 4-6 b_{1u} 3-5 b_{2g} 2-5 b_{3g} 1-3a_u**	**Parusel and Grimme[d]** **MRCI and TDDFT**	**Angeli et al.[e]** **CASSCF (14,13) 6-31G*** **Orbitals in the active space: 3-5 b_{1u} 3-6 b_{2g} 3-6 b_{3g} 1-2 a_u** **State average: 4B_{3u} + 4B_{2u}**
Q bands (Q_x and Q_y)	Described as arising from a configuration interaction among the four "Gouterman's orbitals": b_{1u}, a_u, b_{2g} and b_{3g}. It is essentially a CAS(4,4). See Angeli, Pastore, Cimiraglia (2007) for such a calculation	**1^1B_{2u} and 1^1B_{3u}**: $b_{1u} \rightarrow b_{\{3,2\}g}$ (~50%) $a_u \rightarrow b_{\{3,2\}g}$ (~40%)	**1^1B_{2u} and 1^1B_{3u}**: $b_{1u} \rightarrow b_{\{3,2\}g}$ (~40%) $a_u \rightarrow b_{\{3,2\}g}$ (~35%)	**1^1B_{2u} and 1^1B_{3u}**: $b_{1u} \rightarrow b_{\{3,2\}g}$ (~50%) $a_u \rightarrow b_{\{3,2\}g}$ (~35%)	**1^1B_{2u} and 1^1B_{3u}**: $b_{1u} \rightarrow b_{\{3,2\}g}$ (~43%) $a_u \rightarrow b_{\{3,2\}g}$ (~47%)
B band (Soret band)		**2^1B_{3u}**: $a_u \rightarrow b_{3g}$ (42%) *n*$b_{1u} \rightarrow b_{2g}$ (26%) $b_{1u} \rightarrow b_{2g}$ (20%)	**2^1B_{2u} and 2^1B_{3u}**: $a_u \rightarrow b_{\{2,3\}g}$ (~30%) *n*$b_{1u} \rightarrow b_{\{3,2\}g}$ (~20%) $b_{1u} \rightarrow b_{\{3,2\}g}$ (~15%)	**2^1B_{2u} and 2^1B_{3u}**: $a_u \rightarrow b_{\{2,3\}g}$ (~30%) *n*$b_{1u} \rightarrow b_{\{3,2\}g}$ (~27%) $b_{1u} \rightarrow b_{\{3,2\}g}$ (~15%)	**2^1B_{3u}**: $a_u \rightarrow b_{3g}$ (35%) $b_{1u} \rightarrow b_{2g}$ (25%) *n*$b_{1u} \rightarrow b_{2g}$ (22%) **2^1B_{2u}**: $b_{1u} \rightarrow b_{3g}$ (43%) $a_u \rightarrow b_{3g}$ (37%)

Table SI8. Continuation

	Gouterman (1960s) 4-orbital model[a]	**Tokita et al.[b]** **SAC-CI**	**Serrano-Andrés et al.[c]** **CASSCF (16,14)** **ANO-S C,N [3s2p1d]/H[2s]** **Orbitals in the active space:** **4-6 b_{1u} 3-5 b_{2g}** **2-5 b_{3g} 1-3a_u**	**Parusel and Grimme[d]** **MRCI and TDDFT**	**Angeli et al.[e]** **CASSCF (14,13)** **6-31G*** **Orbitals in the active space:** **3-5 b_{1u} 3-6 b_{2g}** **3-6 b_{3g} 1-2 a_u** **State average:** **4B_{3u} + 4B_{2u}**
N	Not described by the model	**2$^1B_{2u}$**: $b_{1u} \rightarrow b_{3g}$ (41%) $a_u \rightarrow b_{2g}$ (39%) $nb_{1u} \rightarrow b_{3g}$ (8%)	**3$^1B_{3u}$**: $nb_{1u} \rightarrow b_{2g}$ (27%) $b_{1u} \rightarrow b_{2g}$ (13%) $a_u \rightarrow b_{3g}$ (9%) $a_ub_{3g} \rightarrow b_{2g}b_{2g}$ (5%) ---- **3$^1B_{2u}$**: $b_{1u} \rightarrow b_{3g}$ (32%) $nb_{1u} \rightarrow b_{3g}$ (15%) $a_u \rightarrow b_{2g}$ (7%)	**3$^1B_{2u}$ and 3$^1B_{3u}$**: $nb_{1u} \rightarrow b_{\{3,2\}g}$ (~37%) $b_{1u} \rightarrow b_{\{3,2\}g}$ (~15%) $a_u \rightarrow b_{\{3,2\}g}$ (~15%)	**3$^1B_{3u}$**: $b_{1u} \rightarrow b_{2g}$ (37%) $nb_{1u} \rightarrow b_{2g}$ (34%) $a_u \rightarrow b_{3g}$ (9%) --- **3$^1B_{2u}$**: $nb_{1u} \rightarrow b_{3g}$ (56%) $2nb_{1u} \rightarrow b_{3g}$ (20%)
L	Not described by the model	**3$^1B_{3u}$**: $nb_{1u} \rightarrow b_{2g}$ (58%) $a_u \rightarrow b_{3g}$ (16%) $b_{1u} \rightarrow b_{2g}$ (10%) --- **3$^1B_{2u}$**: $b_{1u} \rightarrow b_{3g}$ (79%)	**4$^1B_{3u}$**: $2nb_{1u} \rightarrow b_{2g}$ (55%) $a_unb_{2g} \rightarrow b_{2g}b_{3g}$ (10%) ---- **4$^1B_{2u}$**: $b_{1u} \rightarrow b_{3g}$ (51%) $nb_{1u} \rightarrow b_{3g}$ (6%) $a_ub_{2g} \rightarrow b_{3g}b_{3g}$ (7%)	**4$^1B_{2u}$ and 4$^1B_{3u}$**: $2nb_{1u} \rightarrow b_{\{3,2\}g}$ (~62%) --- **5$^1B_{3u}$**: $b_{3g} \rightarrow a_u$ (37%) $b_{1u}b_{2g} \rightarrow b_{3g}b_{2g}$ (26%)	**4$^1B_{3u}$**: $2nb_{1u} \rightarrow b_{2g}$ (87%) --- **4$^1B_{2u}$**: $nb_{1u} \rightarrow b_{3g}$ (66%) $b_{1u} \rightarrow b_{3g}$ (14%)
M	Not described by the model	**4$^1B_{2u}$ and 4$^1B_{3u}$**: $2nb_{1u} \rightarrow b_{\{3,2\}g}$ (~81%)		**7$^1B_{3u}$**: $a_ub_{3g} \rightarrow b_{2g}$ (19%) $b_{1u}b_{3g} \rightarrow b_{3g}b_{2g}$ (12%)	

a Gouterman *et. al*, *J. Mol. Spectrosc.* **11** (1963); https://doi.org/10.1016/0022-2852(63)90011-0
b Tokita *et. al*, *J. Phys. Chem. A* **102** (1998) 1843; https://doi.org/10.1021/jp9731361
c Serrano-Andrés *et. al*, *Chem. Phys. Lett.* **295** (1998) 195; https://doi.org/10.1016/S0009-2614(98)00934-8
d Parusel and Grimme, *J. Porphyr. Phthalocya.* **5** (2001) 225; https://doi.org/10.1002/jpp.310
e Angeli *et. al*, *Theor. Chem. Acc.* **117** (2007) 743; https://doi.org/10.1007/s00214-006-0207-0

Table SI9. TD-DFT results obtained for the Q-band of CoP. Transition energy (**ΔE**, in eV, in cm^{-1} and the respective wavelength, **λ**, in nm), oscillator strength (***f***) and configurations calculated with different functionals and def2-TZVP basis set

Method	**States**	**Configuration**	**Weight**	**ΔE**			***f* (10^{-4})**
				eV	**cm^{-1}**	**nm**	
BP86	1-B_{2u}	7-b_{1u} → 5-b_{3g}	0.436	2.063	16640.9	600.9	0.002
	1-B_{3u}	7-b_{1u} → 5-b_{2g}	0.436				
	2-B_{2u}	2-a_u → 5-b_{2g}	0.439	2.133	17200.9	581.4	0.490
	2-B_{3u}	2-a_u → 5-b_{3g}	0.439				
OLYP	1-B_{2u}	7-b_{1u} → 5-b_{3g}	0.428	2.072	16713.2	598.3	0.000
	1-B_{3u}	7-b_{1u} → 5-b_{2g}	0.428				
	2-B_{2u}	2-a_u → 5-b_{2g}	0.431	2.135	17219.2	580.7	1.159
	2-B_{3u}	2-a_u → 5-b_{3g}	0.431				
M06-L	1-B_{2u}	2-a_u → 5-b_{2g}	0.330	2.117	17071.6	585.8	0.440
	1-B_{3u}	2-a_u → 5-b_{3g}	0.330				
	2-B_{2u}	7-b_{1u} → 5-b_{3g}	0.334	2.182	17600.9	568.2	0.640
	2-B_{3u}	7-b_{1u} → 5-b_{2g}	0.334				
TPSSh	1-B_{2u}	7-b_{1u} → 5-b_{3g}	0.308	2.072	16715.7	598.2	0.033
	1-B_{3u}	7-b_{1u} → 5-b_{2g}	0.308				
	2-B_{2u}	2-a_u → 5-b_{2g}	0.331	2.173	17528.8	570.5	0.115
	2-B_{3u}	2-a_u → 5-b_{3g}	0.331				

Table SI9. Continuation

Method	States	Configuration	Weight	ΔE			*f (10-4)*
				eV	cm^{-1}	nm	
B3LYP	$1\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.169	2.068	16682.2	599.4	0.054
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.162				
	$1\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.169				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.162				
	$2\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.215	2.172	17520.8	570.7	0.122
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.211				
	$2\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.215				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.221				
PBE0	$1\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.160	2.052	16551.5	604.2	0.055
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.142				
	$1\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.152				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.142				
	$2\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.226	2.189	17651.4	566.5	0.093
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.247				
	$2\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.226				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.247				
M06	$1\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.382	2.031	16385.0	610.3	0.704
	$1\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.382				
	$2\text{-}B_{2u}$	$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.390	2.155	17380.1	575.4	0.505
	$2\text{-}B_{3u}$	$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.390				

Table SI9. Continuation

Method	States	Configuration	Weight	ΔE			*f (10-4)*
				eV	cm^{-1}	nm	
CAM-B3LYP	1-B2u	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.176	1.982	15989.5	625.4	0.065
		$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.132				
	1-B3u	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.132				
		$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.176				
	2-B2u	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.178	2.250	18147.2	551.0	0.076
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.315				
	2-B3u	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.267				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.217				
ωB97X	1-B2u	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.189	1.965	15849.2	630.9	0.114
		$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.121				
	1-B3u	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.121				
		$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.189				
	2-B2u	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.173	2.295	18510.3	540.2	0.185
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.316				
	2-B3u	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.173				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.316				

Table SI10. TD-DFT data obtained for B-band of CoP. Transition energy (**ΔE**, in eV, in cm^{-1} and the respective wavelength, **λ**, in nm), oscillator strength (***f***) and configurations calculated with different functionals and def2-TZVP basis set

Method	States	Configuration	Weight	ΔE			*f*
				eV	cm^{-1}	nm	
BP86	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.249	2.481	20006.7	499.8	0.00380
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.230				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.249				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.230				
OLYP	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.249	2.476	19973.9	500.7	0.00398
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.231				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.233				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.246				
M06-L	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.257	2.531	20415.3	489.8	0.00714
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.226				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.257				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.226				
TPSSh	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.234	2.564	20680.9	483.5	0.00566
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.214				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.234				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.214				
B3LYP	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.237	2.562	20667.7	483.8	0.00740
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.211				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.237				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.211				

Table SI10. Continuation

Method	States	Configuration	Weight	ΔE			*f*
				eV	cm^{-1}	nm	
PBE0	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.243	2.601	20980.5	476.6	0.00860
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.213				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.243				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.213				
M06	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.269	2.510	20247.5	493.9	0.01138
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.233				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.269				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.233				
CAM-B3LYP	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.267	2.595	20933.8	477.7	0.01350
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.217				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.267				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.217				
ωB97X	$3\text{-}B_{2u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{2g}$	0.268	2.578	20790.3	481.0	0.01433
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{3g}$	0.214				
	$3\text{-}B_{3u}$	$2\text{-}a_u \rightarrow 5\text{-}b_{3g}$	0.268				
		$7\text{-}b_{1u} \rightarrow 5\text{-}b_{2g}$	0.214				

Table SI11. TD-DFT data obtained for charge transfer transition of CoP. Transition energy (**ΔE**, in eV, in cm^{-1} and the respective wavelength, **λ**, in nm), oscillator strength (***f***) and configurations calculated with different functionals and def2-TZVP basis set

Method	**States**	**Configuration**	**Type**	**Weight**	**ΔE**			***f***
					eV	**cm^{-1}**	**nm**	
BP86	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	1.000	1.36	10977	911	3.183
	2-B_{1u}	5-b_{1u} → 24-a_g	LMCT	0.999	2.78	22432	446	9.896
	3-B_{1u}	6-b_{1u} → 25-a_g	LMCT	0.991	3.41	27515	363	1.160
	4-B_{1u}	15-b_{1g} → 3-a_u	MLCT	0.999	3.46	27874	359	0.043
OLYP	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.999	1.36	10941	914	2.938
	2-B_{1u}	5-b_{1u} → 24-a_g	LMCT	0.999	2.77	22372	447	9.294
	3-B_{1u}	6-b_{1u} → 25-a_g	LMCT	0.993	3.31	26657	375	1.183
	4-B_{1u}	15-b_{1g} → 3-a_u	MLCT	1.000	3.40	27403	365	0.035
M06-L	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.970	2.32	18685	535	2.992
	2-B_{1u}	6-b_{1u} → 25-a_g	LMCT	0.989	3.76	30362	329	0.386
TPSSh	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	1.000	2.63	21184	472	7.558
B3LYP	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.989	2.95	23774	421	9.399
PBE0	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.984	3.53	28444	352	11.703
M06	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.994	2.69	21725	460	7.654
CAM-B3LYP	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.949	3.60	29010	345	14.315
ωB97X	1-B_{1u}	7-b_{1u} → 24-a_g	LMCT	0.933	3.60	29044	344	19.521

4. Ground and excited states (CASSCF/NEVPT2)

Table SI12. Configurations for the possible CoP ground states. CAS(15,11)/NEVPT2 level of theory using cc-pVTZ-DK basis set. For notation simplification we will adopt the D_{4h} notation only for the $E_{g/u}$ states and orbitals ($B_{2g/u}$ + $B_{3g/u}$ in the D_{2h} notation)

State		Orbital occupation									weight*
		Cobalt Orbitals				Porphyrin Orbitals					
		d_{z2}	d_{x2-y2}	d_{xy}	$d_{xz/yz}$	$2nb_{1u}$	nb_{1u}	b_{1u}^{**}	e_g^{**}	a_u^{**}	
^2A_g		1	0	2	4	2	2	2	0	2	0.89
^2E_g	1	2	0	2	3	2	2	2	0	2	0.82
	2	1	1	2	3	2	2	2	0	2	0.06
$^4B_{1g}$		2	1	2	2	2	2	2	0	2	0.92
^4E_g	1	1	1	2	3	2	2	2	0	2	0.59
	2	2	1	0	3	2	2	2	0	2	0.33

* ≥ 0.05

** Gouterman's orbitals.

Table SI13. Configurations for selected CoP doublet excited states (at the CASSCF (15,11) level of theory) and NEVPT2 energies using cc-pVTZ-DK basis set. E[x→y] $|\Psi\rangle$ indicates the excitation from orbital x to orbital y over configuration $|\Psi\rangle$. Assignments of Q and B bands are indicated. Oscillator strengths (***f***) were calculated with CASSCF transition moments and NEVPT2 transition energies. For notation simplification we will adopt the D_{4h} notation for the $E_{g/u}$ states and orbitals ($B_{2g/u}$+$B_{3g/u}$ in the D_{2h} notation)

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^2A_g \rightarrow {}^2E_u$ (Q-band)	E[$a_u \rightarrow e_g$] $\|{}^2A_g\rangle$	0.59	2.23	17 947	557	9.19e-2
	E[$b_{1u} \rightarrow e_g$] $\|{}^2A_g\rangle$	0.35				
$^2A_g \rightarrow {}^2E_u$ (B-band)	E[$b_{1u} \rightarrow e_g$] $\|{}^2A_g\rangle$	0.50	3.07	24 747	404	2.69
	E[$a_u \rightarrow e_g$] $\|{}^2A_g\rangle$	0.29				
$^2A_g \rightarrow {}^2E_u$	E[$nb_{1u} \rightarrow e_g$] $\|{}^2A_g\rangle$	0.80	3.43	27 644	362	7.10e-2
	E[$2nb_{1u} \rightarrow e_g$] $\|{}^2A_g\rangle$	0.09				
$^2A_g \rightarrow {}^2E_u$	E[$2nb_{1u} \rightarrow e_g$] $\|{}^2A_g\rangle$	0.80	3.71	29 914	334	4.27e-1
	E[$nb_{1u} \rightarrow e_g$] $\|{}^2A_g\rangle$	0.10				
$^2A_g \rightarrow {}^2E_u$	E[$d_{z2}a_u \rightarrow d_{x2-y2}e_g$] $\|{}^2A_g\rangle$	0.43	4.55	36 718	272	2.72e-1
	E[$d_{z2}b_{1u} \rightarrow d_{x2-y2}e_g$] $\|{}^2A_g\rangle$	0.26				
$^2E_g \rightarrow {}^2B_{1u}$[(a)] (Q-band)	E[$a_u \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.50	2.20	17 740	564	3.77e-2
	E[$b_{1u} \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.36				
$^2E_g \rightarrow {}^2B_{1u}$ (Q-band)	E[$a_u \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.54	2.23	17 964	557	4.48e-2
	E[$b_{1u} \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.32				
$^2E_g \rightarrow {}^2B_{1u}$	E[$nb_{1u} \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.68	2.73	22 023	454	8.28e-2
	E[$nb_{1u} \rightarrow d_{xz/yz}$] $\|{}^2E_g\rangle_1$	0.09				
$^2E_g \rightarrow {}^2B_{1u}$ (B-band)	E[$a_u \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.30	2.81	22 685	441	1.26
	E[$b_{1u} \rightarrow e_g$] $\|{}^2E_g\rangle_1$	0.46				

Table SI13. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^2E_g \rightarrow {}^2B_{1u}$ (B-band)	$E[b_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.46	2.95	23 778	421	1.26
	$E[a_u \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.26				
$^2E_g \rightarrow {}^2B_{1u}$	$E[nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.72	3.30	26 634	375	2.68e-2
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.10				
$^2E_g \rightarrow {}^2B_{1u}$	$E[nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.58	3.37	27 216	367	7.02e-2
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.22				
$^2E_g \rightarrow {}^2B_{1u}$	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.68	3.71	29 947	334	2.06e-1
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.10				
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_2$	0.06				
$^2E_g \rightarrow {}^2B_{1u}$	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_2$	0.30	3.73	30 068	333	1.51e-2
	$E[d_{xy}b_{1u} \rightarrow d_{x2\text{-}y2}e_g] \, \vert {}^2E_g\rangle_2$	0.28				
	$E[d_{xy}b_{1u} \rightarrow d_{x2\text{-}y2}e_g] \, \vert {}^2E_g\rangle_1$	0.08				
	$E[d_{xy}nb_{1u} \rightarrow d_{x2\text{-}y2}e_g] \, \vert {}^2E_g\rangle_1$	0.06				
	$E[d_{xy}2nb_{1u} \rightarrow d_{x2\text{-}y2}e_g] \, \vert {}^2E_g\rangle_1$	0.12				
$^2E_g \rightarrow {}^2B_{1u}$	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.72	3.75	30 218	331	2.13e-1
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_1$	0.08				
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_2$	0.06				
$^2E_g \rightarrow {}^2B_{1u}$	$E[d_{xy}b_{1u} \rightarrow d_{x2\text{-}y2}e_g] \, \vert {}^2E_g\rangle_1$	0.58	4.74	38 256	261	4.04e-2
	$E[b_{1u} \rightarrow e_g] \, \vert {}^2E_g\rangle_2$	0.18				

Table SI13. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^2E_g \rightarrow {}^2B_{1u}$	$E[b_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;2}$	0.34	4.94	39 870	251	1.26e-2
	$E[d_{xy}b_{1u} \rightarrow d_{x2\text{-}y2}e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.18				
	$E[d_{xz}d_{yz}b_{1u} \rightarrow d_{x2\text{-}y2}d_{x2\text{-}y2}e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.12				
	$E[2nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.10				
$^2E_g \rightarrow {}^2A_u$ (Q-band)	$E[a_u \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.54	2.19	17 635	567	5.15e-2
	$E[b_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.32				
$^2E_g \rightarrow {}^2A_u$ (Q-band)	$E[a_u \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.54	2.23	17 998	556	4.70e-2
	$E[b_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.32				
$^2E_g \rightarrow {}^2A_u$ (B-band)	$E[b_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.50	2.99	24 076	415	1.38
	$E[a_u \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.28				
$^2E_g \rightarrow {}^2A_u$ (B-band)	$E[b_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.48	3.01	24 252	412	1.31
	$E[a_u \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.24				
$^2E_g \rightarrow {}^2A_u$	$E[nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.74	3.43	27 625	362	2.28e-2
	$E[2nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.08				
	$E[nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;2}$	0.06				
$^2E_g \rightarrow {}^2A_u$	$E[nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.74	3.44	27 726	361	2.41e-2
	$E[2nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.08				
	$E[nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;2}$	0.06				
$^2E_g \rightarrow {}^2A_u$	$E[2nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.74	3.71	29 913	334	2.07e-1
	$E[nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;1}$	0.08				
	$E[2nb_{1u} \rightarrow e_g] \; \vert {}^2E_g\rangle_{\;2}$	0.06				

Table SI13. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^2E_g \rightarrow {}^2A_u$	$E[2nb_{1u} \rightarrow e_g]\ |^2E_g\rangle_1$	0.66	3.87	31 243	320	1.99e-1
	$E[nb_{1u} \rightarrow e_g]\ |^2E_g\rangle_1$	0.08				
	$E[2nb_{1u} \rightarrow e_g]\ |^2E_g\rangle_2$	0.06				
$^2E_g \rightarrow {}^2A_u$	$E[d_{xy}b_{1u} \rightarrow d_{x2\text{-}y2}e_g]\ |^2E_g\rangle_2$	0.64	4.54	36 623	273	1.13e-1
	$E[d_{xy}b_{1u} \rightarrow d_{x2\text{-}y2}e_g]\ |^2E_g\rangle_1$	0.10				
	$E[b_{1u} \rightarrow e_g]\ |^2E_g\rangle_2$	0.06				
$^2E_g \rightarrow {}^2A_u$	$E[a_u \rightarrow e_g]\ |^2E_g\rangle_2$	0.34	5.28	42 579	235	3.06e-2
	$E[d_{xy}a_u \rightarrow d_{x2\text{-}y2}e_g]\ |^2E_g\rangle_1$	0.30				
	$E[d_{xz}d_{yz}b_{1u} \rightarrow d_{x2\text{-}y2}d_{x2\text{-}y2}e_g]\ |^2E_g\rangle_1$	0.16				
$^2E_g \rightarrow {}^2A_u$	$E[a_u \rightarrow e_g]\ |^2E_g\rangle_2$	0.40	5.48	44 205	226	2.23e-2
	$E[d_{xy}a_u \rightarrow d_{x2\text{-}y2}e_g]\ |^2E_g\rangle_1$	0.24				
	$E[d_{xz}d_{yz}b_{1u} \rightarrow d_{x2\text{-}y2}d_{x2\text{-}y2}e_g]\ |^2E_g\rangle_1$	0.16				

* ≥ 0.05

[(a)] The determinants from ^2E_g states are indicated by a subscript index (e.g. $|^2E_g\rangle_1$ and $|^2E_g\rangle_2$) that follows the order from Table SI5.

Table SI14. Configurations for selected CoP quartet excited states (at the CASSCF (15,11) level of theory) and NEVPT2 energies using cc-pVTZ-DK basis set. E[x→y] $|\Psi\rangle$ indicates the excitation from orbital x to orbital y over configuration $|\Psi\rangle$. Assignments of Q and B bands are indicated. Oscillator strengths (***f***) were calculated with CASSCF transition moments and NEVPT2 transition energies. For notation simplification we will adopt the D_{4h} notation only for the $E_{g/u}$ states and orbitals ($B_{2g/u}$+$B_{3g/u}$ in the D_{2h} notation). See also footnotes of Table SI12

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^4B_{1g}\rightarrow{}^4E_u$ (Q-band)	$E[a_u\rightarrow e_g]\ |^4B_{1g}\rangle$	0.58	2.15	17 345	577	8.74e-2
	$E[b_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.37				
$^4B_{1g}\rightarrow{}^4E_u$ (B-band)	$E[b_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.49	3.09	24 907	401	2.33
	$E[a_u\rightarrow e_g]\ |^4B_{1g}\rangle$	0.28				
$^4B_{1g}\rightarrow{}^4E_u$	$E[2nb_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.85	3.46	27 867	359	3.61e-2
	$E[nb_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.06				
$^4B_{1g}\rightarrow{}^4E_u$	$E[b_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.49	3.63	29 265	342	1.65e-1
	$E[d_{xy}d_{x2\text{-}y2}b_{1u}\rightarrow d_{xz}d_{yz}e_g]\ |^4B_{1g}\rangle$	0.32				
	$E[a_u\rightarrow e_g]\ |^4B_{1g}\rangle$	0.05				
$^4B_{1g}\rightarrow{}^4E_u$	$E[2nb_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.83	3.66	29 496	339	4.79e-1
	$E[nb_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.09				
$^4B_{1g}\rightarrow{}^4E_u$	$E[nb_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.62	3.68	29 700	337	5.41e-2
	$E[b_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.13				
	$E[d_{xy}d_{z2}b_{1u}\rightarrow d_{xz}d_{yz}e_g]\ |^4B_{1g}\rangle$	0.11				
	$E[2nb_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.06				
$^4B_{1g}\rightarrow{}^4E_u$	$E[d_{xy}d_{z2}b_{1u}\rightarrow d_{xz}d_{yz}e_g]\ |^4B_{1g}\rangle$	0.54	4.18	33 683	297	4.73e-2
	$E[b_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.33				
$^4B_{1g}\rightarrow{}^4E_u$	$E[b_{1u}\rightarrow e_g]\ |^4B_{1g}\rangle$	0.79	4.35	35 083	285	1.99e-2

Table SI14. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^4B_{1g} \rightarrow {}^4E_u$	$E[d_{xy}d_{z2}b_{1u} \rightarrow d_{xz}d_{yz}e_g] \ |^4B_{1g}\rangle$	0.54	4.39	35 414	282	1.36e-2
	$E[a_u \rightarrow e_g] \ |^4B_{1g}\rangle$	0.33				
$^4B_{1g} \rightarrow {}^4E_u$	$E[a_u \rightarrow e_g] \ |^4B_{1g}\rangle$	0.74	4.45	35 909	278	1.28e-2
$^4B_{1g} \rightarrow {}^4E_u$	$E[a_u \rightarrow e_g] \ |^4B_{1g}\rangle$	0.45	4.74	38 244	261	2.53e-1
	$E[d_{xy}d_{z2}a_u \rightarrow d_{xz}d_{yz}e_g] \ |^4B_{1g}\rangle$	0.43				
$^4B_{1g} \rightarrow {}^4E_u$	$E[d_{z2}d_{z2}a_u \rightarrow d_{xz}d_{yz}e_g] \ |^4B_{1g}\rangle$	0.69	4.75	38 273	261	8.87e-3
	$E[a_u \rightarrow e_g] \ |^4B_{1g}\rangle$	0.09				
	$E[d_{xy}d_{xy}a_u \rightarrow d_{xz}d_{yz}e_g] \ |^4B_{1g}\rangle$	0.06				
	$E[d_{xy}a_u \rightarrow d_{x2\text{-}y2}e_g] \ |^4B_{1g}\rangle$	0.05				
$^4E_g \rightarrow {}^4B_{1u}$ [(a)] (Q-band)	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_{\ 1}$	0.36	2.18	17 609	568	3.78e-2
	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_{\ 1}$	0.26				
	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_{\ 2}$	0.20				
	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_{\ 2}$	0.14				
$^4E_g \rightarrow {}^4B_{1u}$ (Q-band)	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_{\ 1}$	0.38	2.22	17 878	559	4.74e-2
	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_{\ 2}$	0.24				
	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_{\ 1}$	0.20				
	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_{\ 2}$	0.12				

Table SI14. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^4E_g \rightarrow {}^4B_{1u}$ (B-band)	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.32	2.95	23 830	420	1.25
	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_1$	0.26				
	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.16				
	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_2$	0.10				
$^4E_g \rightarrow {}^4B_{1u}$ (B-band)	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.34	2.99	24 118	415	1.34
	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_1$	0.22				
	$E[b_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.20				
	$E[a_u \rightarrow e_g] \ |^4E_g\rangle_2$	0.10				
$^4E_g \rightarrow {}^4B_{1u}$	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.56	3.17	25 546	391	1.24e-2
	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.28				
	$E[2nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.08				
$^4E_g \rightarrow {}^4B_{1u}$	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.56	3.31	26 715	374	3.18e-2
	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.26				
	$E[2nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.08				
$^4E_g \rightarrow {}^4B_{1u}$	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.52	3.41	27 509	364	6.61e-2
	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.26				
	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.10				
$^4E_g \rightarrow {}^4B_{1u}$	$E[2nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.46	3.63	29 297	341	1.58e-2
	$E[2nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.18				
	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_2$	0.08				
	$E[d_{z2}b_{1u} \rightarrow d_{x2-y2}e_g] \ |^4E_g\rangle_2$	0.08				
	$E[nb_{1u} \rightarrow e_g] \ |^4E_g\rangle_1$	0.06				

Table SI14. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^4E_g \rightarrow {}^4B_{1u}$	$E[2nb_{1u} \rightarrow e_g]\ |^4E_g\rangle_1$	0.54	3.63	29 313	341	2.19e-1
	$E[2nb_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.26				
	$E[nb_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.08				
$^4E_g \rightarrow {}^4B_{1u}$	$E[2nb_{1u} \rightarrow e_g]\ |^4E_g\rangle_1$	0.54	3.70	29 879	335	2.23e-1
	$E[2nb_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.30				
	$E[nb_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.06				
$^4E_g \rightarrow {}^4B_{1u}$	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_1$	0.62	4.31	34 740	288	2.50e-2
	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.22				
$^4E_g \rightarrow {}^4B_{1u}$	$E[d_{xy}a_u \rightarrow d_{x2\text{-}y2}e_g]\ |^4E_g\rangle_1$	0.66	5.03	40 570	246	2.15e-2
	$E[a_u \rightarrow e_g]\ |^4E_g\rangle_2$	0.12				
	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_1$	0.08				
$^4E_g \rightarrow {}^4A_u$ (Q-band)	$E[a_u \rightarrow e_g]\ |^4E_g\rangle_1$	0.38	2.19	17 642	567	5.04e-2
	$E[a_u \rightarrow e_g]\ |^4E_g\rangle_2$	0.24				
	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_1$	0.22				
	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.12				
$^4E_g \rightarrow {}^4A_u$ (Q-band)	$E[a_u \rightarrow e_g]\ |^4E_g\rangle_1$	0.38	2.20	17 754	563	4.13e-2
	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_1$	0.24				
	$E[a_u \rightarrow e_g]\ |^4E_g\rangle_2$	0.22				
	$E[b_{1u} \rightarrow e_g]\ |^4E_g\rangle_2$	0.14				

Table SI14. Continuation

Transition	Excitation	weight*	Energy			*f*
			eV	cm^{-1}	nm	
$^4E_g \rightarrow {}^4A_u$ (B-band)	$E[b_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.34	2.93	23 636	423	1.34
	$E[b_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.20				
	$E[a_u \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.18				
	$E[a_u \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.14				
$^4E_g \rightarrow {}^4A_u$ (B-band)	$E[b_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.36	3.01	24 307	411	1.35
	$E[a_u \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.20				
	$E[b_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.18				
	$E[a_u \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.12				
$^4E_g \rightarrow {}^4A_u$	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.52	3.36	27 099	369	2.06e-2
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.34				
$^4E_g \rightarrow {}^4A_u$	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.52	3.42	27 574	363	3.43e-2
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.32				
$^4E_g \rightarrow {}^4A_u$	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.36	3.61	29 119	343	8.75e-3
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.30				
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.08				
$^4E_g \rightarrow {}^4A_u$	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.48	3.67	29 598	338	2.27e-1
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.34				
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.10				
$^4E_g \rightarrow {}^4A_u$	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.52	3.71	29 918	334	2.23e-1
	$E[2nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.32				
	$E[nb_{1u} \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.08				
$^4E_g \rightarrow {}^4A_u$	$E[a_u \rightarrow e_g] \, \vert {}^4E_g\rangle_1$	0.62	4.42	35 632	281	5.67e-2
	$E[a_u \rightarrow e_g] \, \vert {}^4E_g\rangle_2$	0.24				

Table SI15. Transitions energies (in eV) and oscillator strength (***f***) dependence with the basis set cardinality. CAS(15,11)/NEVPT2 level of theory using cc-pVnZ-DK basis set. The transitions were ordered based on the reference wavefunction, these had small changes with the basis set increasing. For notation simplification we will adopt the D_{4h} notation only for the $E_{g/u}$ states ($B_{2g/u}$ + $B_{3g/u}$ in the D_{2h} notation)

Transition	**cc-pVDZ-DK**		**cc-pVTZ-DK**		**cc-pVQZ-DK**	
	Energy	***f***	**Energy**	***f***	**Energy**	***f***
$^2A_g \rightarrow {}^2E_g$	2.28	9.11e-2	2.23	9.19e-2	2.22	9.10e-2
$^2A_g \rightarrow {}^2E_g$	3.59	2.31	3.07	2.69	3.02	2.72
$^2A_g \rightarrow {}^2E_g$	3.54	7.69e-2	3.43	7.10e-2	3.41	6.72e-2
$^2A_g \rightarrow {}^2E_g$	3.89	4.51e-1	3.71	4.27e-1	3.67	4.24e-1
$^2A_g \rightarrow {}^2E_g$	4.24	1.21	4.55	2.72e-1	4.55	1.95e-1
$^2E_g \rightarrow {}^2B_{1u}$	2.25	3.70e-2	2.20	3.77e-2		
$^2E_g \rightarrow {}^2B_{1u}$	2.28	4.44e-2	2.23	4.48e-2		
$^2E_g \rightarrow {}^2B_{1u}$	2.81	1.23e-1	2.73	8.28e-2		
$^2E_g \rightarrow {}^2B_{1u}$	2.90	1.29	2.81	1.26		
$^2E_g \rightarrow {}^2B_{1u}$	3.04	1.17	2.95	1.26		
$^2E_g \rightarrow {}^2B_{1u}$	3.23	1.82e-2	3.30	2.68e-2		
$^2E_g \rightarrow {}^2B_{1u}$	3.48	2.99e-2	3.37	7.02e-2		
$^2E_g \rightarrow {}^2B_{1u}$	3.60	7.16e-2	3.71	2.06e-1		
$^2E_g \rightarrow {}^2B_{1u}$	3.74	7.66e-3	3.73	1.51e-2		
$^2E_g \rightarrow {}^2B_{1u}$	3.89	2.27e-1	3.75	2.13e-1		
$^2E_g \rightarrow {}^2B_{1u}$	4.63	8.40e-3	4.74	4.04e-2		
$^2E_g \rightarrow {}^2B_{1u}$	4.92	9.51e-3	4.94	1.26e-2		

Table SI15. Continuation

Transition	cc-pVDZ-DK		cc-pVTZ-DK		cc-pVQZ-DK	
	Energy	***f***	**Energy**	***f***	**Energy**	***f***
$^2E_g \rightarrow {}^2A_u$	2.24	5.18e-2	2.19	5.15e-2		
$^2E_g \rightarrow {}^2A_u$	2.29	4.66e-2	2.23	4.70e-2		
$^2E_g \rightarrow {}^2A_u$	3.04	1.36	2.99	1.38		
$^2E_g \rightarrow {}^2A_u$	3.14	1.41	03.01	1.31		
$^2E_g \rightarrow {}^2A_u$	3.55	2.51e-2	3.43	2.28e-2		
$^2E_g \rightarrow {}^2A_u$	3.61	2.62e-2	3.44	2.41e-2		
$^2E_g \rightarrow {}^2A_u$	3.88	2.17e-1	3.71	2.07e-1		
$^2E_g \rightarrow {}^2A_u$	3.94	2.19e-1	3.87	1.99e-1		
$^2E_g \rightarrow {}^2A_u$	4.76	2.02e-2	4.54	1.13e-1		
$^2E_g \rightarrow {}^2A_u$	5.37	9.04e-2	5.28	3.06e-2		
$^2E_g \rightarrow {}^2A_u$	5.61	3.54e-2	5.48	2.23e-2		
$^4B_{1g} \rightarrow {}^4E_u$	2.20	8.65e-2	2.15	8.74e-2		
$^4B_{1g} \rightarrow {}^4E_u$	3.19	2.38	3.09	2.33		
$^4B_{1g} \rightarrow {}^4E_u$	3.11	2.59e-3	3.46	3.61e-2		
$^4B_{1g} \rightarrow {}^4E_u$	3.60	4.00e-2	3.63	1.65e-1		
$^4B_{1g} \rightarrow {}^4E_u$	3.74	1.46e-1	3.66	4.79e-1		
$^4B_{1g} \rightarrow {}^4E_u$	3.84	5.07e-1	3.68	5.41e-2		
$^4B_{1g} \rightarrow {}^4E_u$	4.29	6.46e-2	4.18	4.73e-2		
$^4B_{1g} \rightarrow {}^4E_u$	4.46	2.51e-2	4.35	1.99e-2		
$^4B_{1g} \rightarrow {}^4E_u$	4.50	1.68e-2	4.39	1.36e-2		

Table SI15. Continuation

Transition	cc-pVDZ-DK		cc-pVTZ-DK		cc-pVQZ-DK	
	Energy	***f***	**Energy**	***f***	**Energy**	***f***
$^4B_{1g} \rightarrow {}^4E_u$	4.57	1.28e-1	4.45	1.28e-2		
$^4B_{1g} \rightarrow {}^4E_u$	4.88	2.77e-1	4.74	2.53e-1		
$^4B_{1g} \rightarrow {}^4E_u$	4.90	3.55e-3	4.75	8.87e-3		
$^4E_g \rightarrow {}^4B_{1u}$	2.28	4.70e-2	2.18	3.78e-2		
$^4E_g \rightarrow {}^4B_{1u}$	2.24	3.70e-2	2.22	4.74e-2		
$^4E_g \rightarrow {}^4B_{1u}$	3.05	1.27	2.95	1.25		
$^4E_g \rightarrow {}^4B_{1u}$	3.09	1.37	2.99	1.34		
$^4E_g \rightarrow {}^4B_{1u}$	3.26	1.62e-2	3.17	1.24e-2		
$^4E_g \rightarrow {}^4B_{1u}$	3.42	3.43e-2	3.31	3.18e-2		
$^4E_g \rightarrow {}^4B_{1u}$	3.53	7.24e-2	3.41	6.61e-2		
$^4E_g \rightarrow {}^4B_{1u}$	3.65	1.65e-2	3.63	1.58e-2		
$^4E_g \rightarrow {}^4B_{1u}$	3.81	2.32e-1	3.63	2.19e-1		
$^4E_g \rightarrow {}^4B_{1u}$	3.88	2.37e-1	3.70	2.23e-1		
$^4E_g \rightarrow {}^4B_{1u}$	4.42	2.91e-2	4.31	2.50e-2		
$^4E_g \rightarrow {}^4B_{1u}$	5.18	2.76e-2	5.03	2.15e-2		
$^4E_g \rightarrow {}^4A_u$	2.25	5.07e-2	2.19	5.04e-2		
$^4E_g \rightarrow {}^4A_u$	2.26	4.09e-2	2.20	4.13e-2		
$^4E_g \rightarrow {}^4A_u$	03.03	1.37	2.93	1.34		
$^4E_g \rightarrow {}^4A_u$	3.11	1.38	03.01	1.35		
$^4E_g \rightarrow {}^4A_u$	3.47	2.23e-2	3.36	2.06e-2		

Table SI15. Continuation

Transition	cc-pVDZ-DK		cc-pVTZ-DK		cc-pVQZ-DK	
	Energy	***f***	**Energy**	***f***	**Energy**	***f***
$^4E_g \rightarrow {}^4A_u$	3.54	3.59e-2	3.42	3.43e-2		
$^4E_g \rightarrow {}^4A_u$	3.80	9.51e-3	3.61	8.75e-3		
$^4E_g \rightarrow {}^4A_u$	3.85	2.40e-1	3.67	2.27e-1		
$^4E_g \rightarrow {}^4A_u$	3.89	2.36e-1	3.71	2.23e-1		
$^4E_g \rightarrow {}^4A_u$	4.55	5.00e-2	4.42	5.67e-2		