

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

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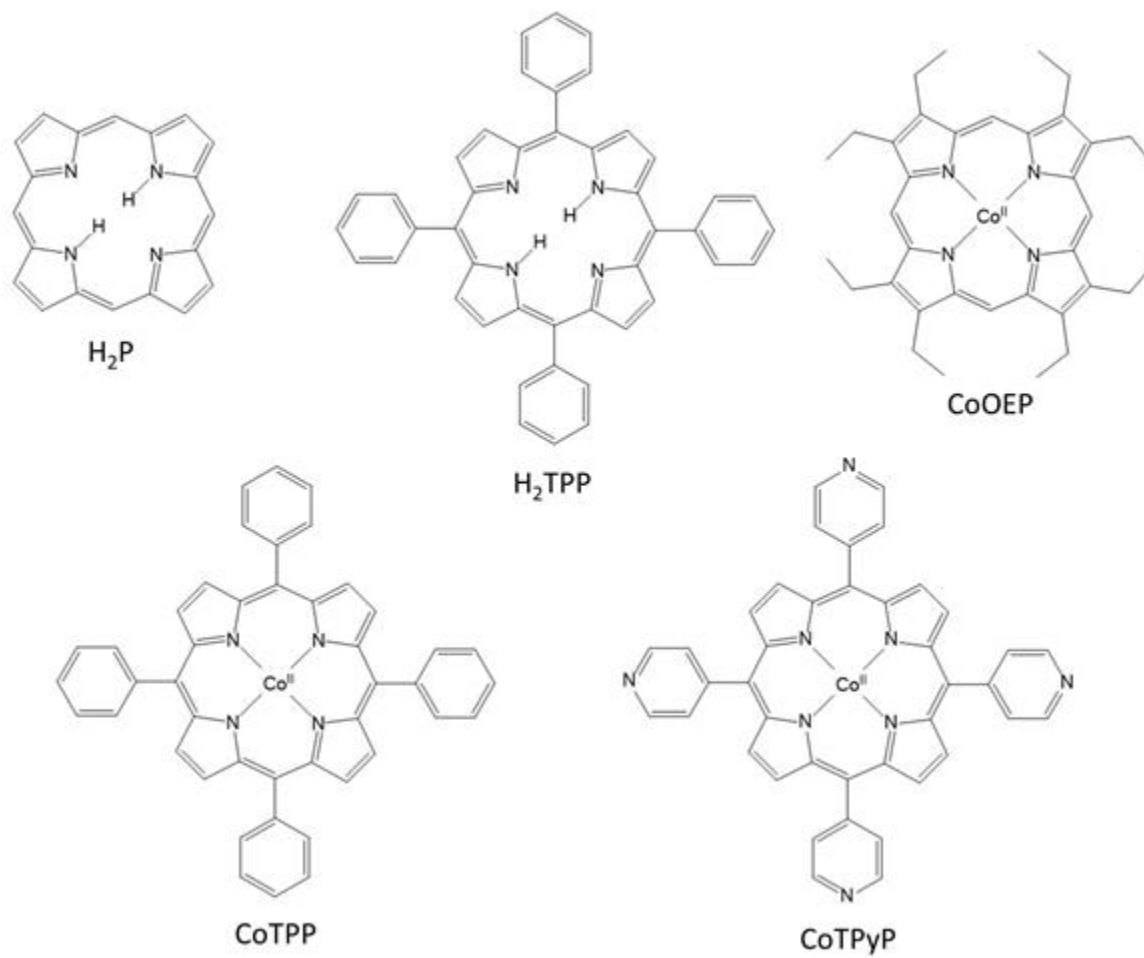
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### **SUPPLEMENTARY INFORMATION**

## 1. Reference data



**Figure S11.** Molecular structure of the derivatives used as comparison.

**Table SI1.** Experimental spectrophotometry data for Q-band of H<sub>2</sub>P, H<sub>2</sub>TPP, CoTPP and CoTPyP

Molecule	Solvent	T (°C)	Q(0-0) (nm)	Q(1-0) (nm)	$\epsilon$ (cm <sup>-1</sup> M <sup>-1</sup> )	Ref.
H <sub>2</sub> P	Vapor	393	627.5 (x)	575.0 (x)	-	<i>a</i>
	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 <sub>2</sub> TPP	Vapor	448	664.0 (x)	602.5 (x)	-	<i>b</i>
	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 <sub>2</sub> TPP	Dichloro-Methane	-	620	585	
Dichloro-Methane		538		514	-	

**Table S11:** continuation

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

*a* Edwards et. al, *J. Mol. Spec.* **38** (1971) 16; [https://doi.org/10.1016/0022-2852\(71\)90090-7](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

<sup>#</sup> Values obtained by deconvolution method using Voigt functions

**Table S12.** Experimental spectrophotometry data for B-band (Soret band) of H<sub>2</sub>P, H<sub>2</sub>TPP, CoTPP and CoTPyP

Molecules	Solvent	T (°C)	B (nm)	$\epsilon$ (cm <sup>-1</sup> M <sup>-1</sup> )	Ref.
H <sub>2</sub> P	Vapor	322	372.5	-	<i>a</i>
	Benzene	25	396.5	-	
	Ethanol	-180	390.6	-	
	Dichloro-Methane	25	393.5	-	
H <sub>2</sub> TPP	Vapor	395	402.5	-	<i>b</i>
	Benzene	25	418.5	-	
	Oil	294	419.0	-	
	Oil	32	418.0	-	
	DMOE	25	415.0	-	
	Dichloro-Methane	25	416.0	-	
H <sub>2</sub> TPP	Dichloro-Methane	-	417.0	-	<i>f</i>
CoTTP	Vapor	393	398.5	-	<i>a</i>
	Benzene	25	414.6	-	
	Dichloro-Methane	25	404.0	-	
CoTTP	Benzene	45	412.0	0.002900	<i>b</i>
	Toluene	45	412.0	0.002600	
	Dichloro-Methane	23	410.0	0.002900	<i>c</i>
CoTPP	Pyridine	-	409.0	0.001800	<i>d</i>
	PhCN	-	417.0	0.002360	
	Dichloro-Methane	-	411.0	0.002100	
CoTPP	PhCN	22	416.8	0.001785	<i>e</i>
CoTPP	Dichloro-Methane	-	410.0	-	<i>f</i>
CoTPyP	Chloroform/Methanol	-	411.0	-	<i>g</i>

*a* Edwards et. al, J Mol Spec. **38** (1971) 16; [https://doi.org/10.1016/0022-2852\(71\)90090-7](https://doi.org/10.1016/0022-2852(71)90090-7)

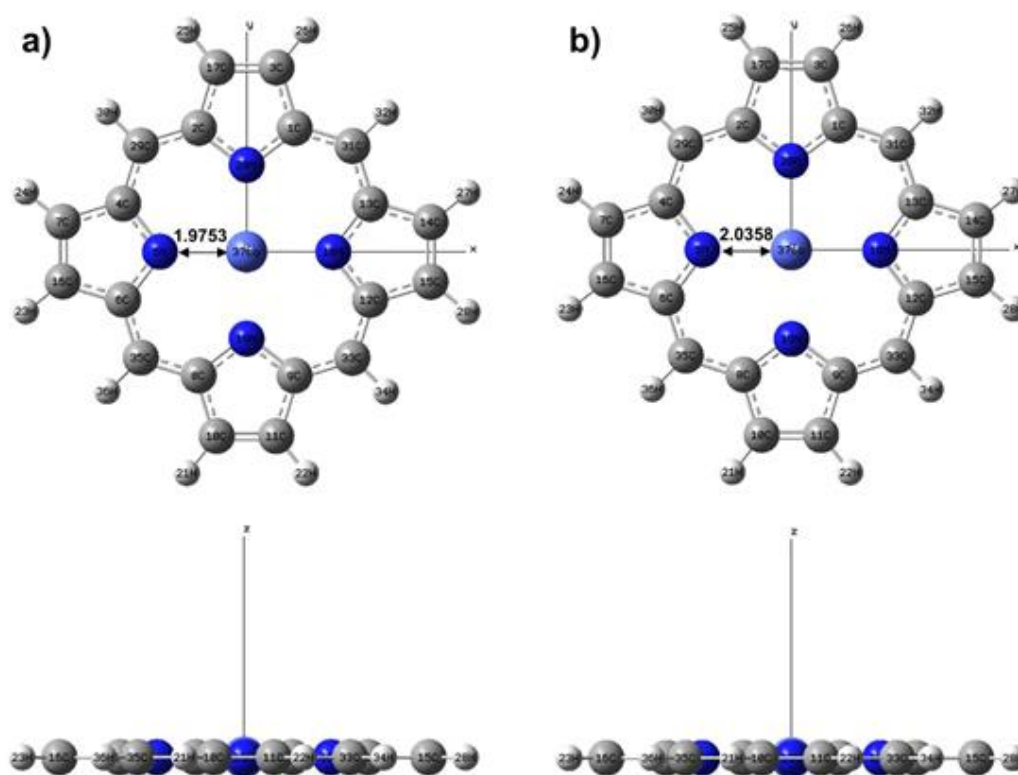
*b* Mu et. al, Electroanalysis **1** (1989) 113; <https://doi.org/10.1002/elan.1140010205>

*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 S13.** 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- $\zeta$  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	$\omega$ B97X
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 <sup>(b)</sup>	2.21 - 2.41 eV <sup>(b)</sup>
Q(1-0) band	2.23 - 2.43 eV <sup>(a)</sup>	2.38 - 2.61 eV <sup>(b)</sup>
B band	3.01 - 3.22 eV <sup>(a)</sup>	3.16 - 3.40 eV <sup>(b)</sup>
M band	6.20 eV (CoTTP and FBTPP) <sup>(a)</sup>	5.51 eV (free base) <sup>(a)</sup>
unnamed band 2	4.72 eV <sup>(a)</sup>	
unnamed band 1	1.61 eV <sup>(a)</sup>	

(a) experimental data from Edwards *et. al*, *J. Mol. Spec.* **38** (1971) 16; [https://doi.org/10.1016/0022-2852\(71\)90090-7](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<sub>4h</sub>, 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](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;
- $nb_{1u}$  is the HOMO-1 of that symmetry;
- $2nb_{1u}$  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 S18.** Bands classification for a free-base porphyrin absorption spectrum as presented by Gouterman and selected wave function calculations

	<b>Gouterman (1960s) 4-orbital model<sup>a</sup></b>	<b>Tokita et al.<sup>b</sup> SAC-CI</b>	<b>Serrano-Andrés et al.<sup>c</sup> CASSCF (16,14) ANO-S C,N [3s2p1d]/H[2s]</b>	<b>Parusel and Grimme<sup>d</sup> MRCI and TDDFT</b>	<b>Angeli et al.<sup>e</sup> CASSCF (14,13) 6-31G*</b>
			<b>Orbitals in the active space:</b> 4-6 $b_{1u}$ 3-5 $b_{2g}$ 2-5 $b_{3g}$ 1-3 $a_u$		<b>Orbitals in the active space:</b> 3-5 $b_{1u}$ 3-6 $b_{2g}$ 3-6 $b_{3g}$ 1-2 $a_u$
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, Cimiraaglia (2007) for such a calculation	<b>1<sup>1</sup>B<sub>2u</sub> and 1<sup>1</sup>B<sub>3u</sub>:</b> $b_{1u} \rightarrow b_{\{3,2\}g}$ (~50%) $a_u \rightarrow b_{\{3,2\}g}$ (~40%)	<b>1<sup>1</sup>B<sub>2u</sub> and 1<sup>1</sup>B<sub>3u</sub>:</b> $b_{1u} \rightarrow b_{\{3,2\}g}$ (~40%) $a_u \rightarrow b_{\{3,2\}g}$ (~35%)	<b>1<sup>1</sup>B<sub>2u</sub> and 1<sup>1</sup>B<sub>3u</sub>:</b> $b_{1u} \rightarrow b_{\{3,2\}g}$ (~50%) $a_u \rightarrow b_{\{3,2\}g}$ (~35%)	<b>1<sup>1</sup>B<sub>2u</sub> and 1<sup>1</sup>B<sub>3u</sub>:</b> $b_{1u} \rightarrow b_{\{3,2\}g}$ (~43%) $a_u \rightarrow b_{\{3,2\}g}$ (~47%)
B band (Soret band)		<b>2<sup>1</sup>B<sub>3u</sub>:</b> $a_u \rightarrow b_{3g}$ (42%) $nb_{1u} \rightarrow b_{2g}$ (26%) $b_{1u} \rightarrow b_{2g}$ (20%)	<b>2<sup>1</sup>B<sub>2u</sub> and 2<sup>1</sup>B<sub>3u</sub>:</b> $a_u \rightarrow b_{\{2,3\}g}$ (~30%) $nb_{1u} \rightarrow b_{\{3,2\}g}$ (~20%) $b_{1u} \rightarrow b_{\{3,2\}g}$ (~15%)	<b>2<sup>1</sup>B<sub>2u</sub> and 2<sup>1</sup>B<sub>3u</sub>:</b> $a_u \rightarrow b_{\{2,3\}g}$ (~30%) $nb_{1u} \rightarrow b_{\{3,2\}g}$ (~27%) $b_{1u} \rightarrow b_{\{3,2\}g}$ (~15%)	<b>2<sup>1</sup>B<sub>3u</sub>:</b> $a_u \rightarrow b_{3g}$ (35%) $b_{1u} \rightarrow b_{2g}$ (25%) $nb_{1u} \rightarrow b_{2g}$ (22%)
					<b>2<sup>1</sup>B<sub>2u</sub>:</b> $b_{1u} \rightarrow b_{3g}$ (43%) $a_u \rightarrow b_{3g}$ (37%)

Table SI8. Continuation

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

a Gouterman et. al, *J. Mol. Spectrosc.* **11** (1963); [https://doi.org/10.1016/0022-2852\(63\)90011-0](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](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 S19.** TD-DFT results obtained for the Q-band of CoP. Transition energy ( $\Delta E$ , in eV, in  $\text{cm}^{-1}$  and the respective wavelength,  $\lambda$ , in nm), oscillator strength ( $f$ ) and configurations calculated with different functionals and def2-TZVP basis set

Method	States	Configuration	Weight	$\Delta E$			$f (10^{-4})$
				eV	$\text{cm}^{-1}$	nm	
BP86	1-B <sub>2u</sub>	7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.436	2.063	16640.9	600.9	0.002
	1-B <sub>3u</sub>	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.436				
	2-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.439	2.133	17200.9	581.4	0.490
	2-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.439				
OLYP	1-B <sub>2u</sub>	7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.428	2.072	16713.2	598.3	0.000
	1-B <sub>3u</sub>	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.428				
	2-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.431	2.135	17219.2	580.7	1.159
	2-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.431				
M06-L	1-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.330	2.117	17071.6	585.8	0.440
	1-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.330				
	2-B <sub>2u</sub>	7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.334	2.182	17600.9	568.2	0.640
	2-B <sub>3u</sub>	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.334				
TPSSH	1-B <sub>2u</sub>	7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.308	2.072	16715.7	598.2	0.033
	1-B <sub>3u</sub>	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.308				
	2-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.331	2.173	17528.8	570.5	0.115
	2-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.331				

**Table S19.** Continuation

Method	States	Configuration	Weight	$\Delta E$			$f(10^{-4})$				
				eV	cm <sup>-1</sup>	nm					
B3LYP	1-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.169	2.068	16682.2	599.4	0.054				
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.162								
	1-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.169								
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.162								
	2-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.215					2.172	17520.8	570.7	0.122
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.211								
2-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.215									
	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.221									
PBE0	1-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.160	2.052	16551.5	604.2	0.055				
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.142								
	1-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.152								
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.142								
	2-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.226					2.189	17651.4	566.5	0.093
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.247								
2-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.226									
	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.247									
M06	1-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.382	2.031	16385.0	610.3	0.704				
	1-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.382								
	2-B <sub>2u</sub>	7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.390	2.155	17380.1	575.4	0.505				
	2-B <sub>3u</sub>	7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.390								

**Table S19.** Continuation

Method	States	Configuration	Weight	$\Delta E$			$f(10^{-4})$	
				eV	$\text{cm}^{-1}$	nm		
CAM-B3LYP	1-B2u	$2-a_u \rightarrow 5-b_{2g}$	0.176	1.982	15989.5	625.4	0.065	
		$2-a_u \rightarrow 5-b_{3g}$	0.132					
	1-B3u	$2-a_u \rightarrow 5-b_{2g}$	0.132					
		$2-a_u \rightarrow 5-b_{3g}$	0.176					
	2-B2u	$2-a_u \rightarrow 5-b_{2g}$	0.178	2.250	18147.2	551.0	0.076	
		$7-b_{1u} \rightarrow 5-b_{3g}$	0.315					
		2-B3u	$2-a_u \rightarrow 5-b_{3g}$					0.267
			$7-b_{1u} \rightarrow 5-b_{2g}$					0.217
$\omega$ B97X	1-B2u	$2-a_u \rightarrow 5-b_{2g}$	0.189	1.965	15849.2	630.9	0.114	
		$2-a_u \rightarrow 5-b_{3g}$	0.121					
	1-B3u	$2-a_u \rightarrow 5-b_{2g}$	0.121					
		$2-a_u \rightarrow 5-b_{3g}$	0.189					
	2-B2u	$2-a_u \rightarrow 5-b_{2g}$	0.173	2.295	18510.3	540.2	0.185	
		$7-b_{1u} \rightarrow 5-b_{3g}$	0.316					
		2-B3u	$2-a_u \rightarrow 5-b_{3g}$					0.173
			$7-b_{1u} \rightarrow 5-b_{2g}$					0.316

**Table S110.** TD-DFT data obtained for B-band of CoP. Transition energy ( $\Delta E$ , in eV, in  $\text{cm}^{-1}$  and the respective wavelength,  $\lambda$ , in nm), oscillator strength ( $f$ ) and configurations calculated with different functionals and def2-TZVP basis set

Method	States	Configuration	Weight	$\Delta E$			$f$
				eV	$\text{cm}^{-1}$	nm	
BP86	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.249	2.481	20006.7	499.8	0.00380
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.230				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.249				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.230				
OLYP	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.249	2.476	19973.9	500.7	0.00398
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.231				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.233				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.246				
M06-L	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.257	2.531	20415.3	489.8	0.00714
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.226				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.257				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.226				
TPSSH	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.234	2.564	20680.9	483.5	0.00566
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.214				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.234				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.214				
B3LYP	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.237	2.562	20667.7	483.8	0.00740
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.211				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.237				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.211				

**Table SI10.** Continuation

Method	States	Configuration	Weight	$\Delta E$			$f$
				eV	cm <sup>-1</sup>	nm	
PBE0	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.243	2.601	20980.5	476.6	0.00860
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.213				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.243				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.213				
M06	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.269	2.510	20247.5	493.9	0.01138
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.233				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.269				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.233				
CAM-B3LYP	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.267	2.595	20933.8	477.7	0.01350
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.217				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.267				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.217				
$\omega$ B97X	3-B <sub>2u</sub>	2-a <sub>u</sub> → 5-b <sub>2g</sub>	0.268	2.578	20790.3	481.0	0.01433
		7-b <sub>1u</sub> → 5-b <sub>3g</sub>	0.214				
	3-B <sub>3u</sub>	2-a <sub>u</sub> → 5-b <sub>3g</sub>	0.268				
		7-b <sub>1u</sub> → 5-b <sub>2g</sub>	0.214				



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

Method	States	Configuration	Type	Weight	$\Delta E$			$f$
					eV	$\text{cm}^{-1}$	nm	
BP86	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	1.000	1.36	10977	911	3.183
	2-B <sub>1u</sub>	5-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.999	2.78	22432	446	9.896
	3-B <sub>1u</sub>	6-b <sub>1u</sub> → 25-a <sub>g</sub>	LMCT	0.991	3.41	27515	363	1.160
	4-B <sub>1u</sub>	15-b <sub>1g</sub> → 3-a <sub>u</sub>	MLCT	0.999	3.46	27874	359	0.043
OLYP	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.999	1.36	10941	914	2.938
	2-B <sub>1u</sub>	5-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.999	2.77	22372	447	9.294
	3-B <sub>1u</sub>	6-b <sub>1u</sub> → 25-a <sub>g</sub>	LMCT	0.993	3.31	26657	375	1.183
	4-B <sub>1u</sub>	15-b <sub>1g</sub> → 3-a <sub>u</sub>	MLCT	1.000	3.40	27403	365	0.035
M06-L	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.970	2.32	18685	535	2.992
	2-B <sub>1u</sub>	6-b <sub>1u</sub> → 25-a <sub>g</sub>	LMCT	0.989	3.76	30362	329	0.386
TPSSh	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	1.000	2.63	21184	472	7.558
B3LYP	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.989	2.95	23774	421	9.399
PBE0	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.984	3.53	28444	352	11.703
M06	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.994	2.69	21725	460	7.654
CAM-B3LYP	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	LMCT	0.949	3.60	29010	345	14.315
$\omega$ B97X	1-B <sub>1u</sub>	7-b <sub>1u</sub> → 24-a <sub>g</sub>	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						
	$d_{z^2}$	$d_{x^2-y^2}$	$d_{xy}$	$d_{xz/yz}$	$2nb_{1u}$	$nb_{1u}$	$b_{1u}^{**}$	$e_g^{**}$	$a_u^{**}$		
$^2A_g$	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

\*  $\geq 0.05$

\*\* 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.  $E[x \rightarrow y] |\Psi\rangle$  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 <sup>-1</sup>	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				
${}^2A_g \rightarrow {}^2E_u$	$E[d_{z^2}a_u \rightarrow d_{x^2-y^2}e_g]   {}^2A_g \rangle$	0.43	4.55	36 718	272	2.72e-1
	$E[d_{z^2}b_{1u} \rightarrow d_{x^2-y^2}e_g]   {}^2A_g \rangle$	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			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.46	2.95	23 778	421	1.26
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.26				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.72	3.30	26 634	375	2.68e-2
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.10				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.58	3.37	27 216	367	7.02e-2
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.22				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.68	3.71	29 947	334	2.06e-1
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.10				
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.30	3.73	30 068	333	1.51e-2
	E[d <sub>xy</sub> b <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.28				
	E[d <sub>xy</sub> b <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
	E[d <sub>xy</sub> nb <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.06				
	E[d <sub>xy</sub> 2nb <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.12				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.72	3.75	30 218	331	2.13e-1
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[d <sub>xy</sub> b <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.58	4.74	38 256	261	4.04e-2
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.18				

**Table SI13.** Continuation

Transition	Excitation	weight*	Energy			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> B <sub>1u</sub>	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.34	4.94	39 870	251	1.26e-2
	E[d <sub>xy</sub> b <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.18				
	E[d <sub>xz</sub> d <sub>yz</sub> b <sub>1u</sub> →d <sub>x<sup>2</sup>-y<sup>2</sup></sub> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.12				
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.10				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub> (Q-band)	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.54	2.19	17 635	567	5.15e-2
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.32				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub> (Q-band)	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.54	2.23	17 998	556	4.70e-2
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.32				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.50	2.99	24 076	415	1.38
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.28				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.48	3.01	24 252	412	1.31
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.24				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.74	3.43	27 625	362	2.28e-2
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.74	3.44	27 726	361	2.41e-2
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.74	3.71	29 913	334	2.07e-1
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				

**Table SI13.** Continuation

Transition	Excitation	weight*	Energy			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[2nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.66	3.87	31 243	320	1.99e-1
	E[nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
	E[2nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[d <sub>xy</sub> b <sub>1u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.64	4.54	36 623	273	1.13e-1
	E[d <sub>xy</sub> b <sub>1u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.10				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.34	5.28	42 579	235	3.06e-2
	E[d <sub>xy</sub> a <sub>u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.30				
	E[d <sub>xz</sub> d <sub>yz</sub> b <sub>1u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.16				
<sup>2</sup> E <sub>g</sub> → <sup>2</sup> A <sub>u</sub>	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.40	5.48	44 205	226	2.23e-2
	E[d <sub>xy</sub> a <sub>u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.24				
	E[d <sub>xz</sub> d <sub>yz</sub> b <sub>1u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>2</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.16				

\* ≥ 0.05

(a) The determinants from <sup>2</sup>E<sub>g</sub> states are indicated by a subscript index (e.g. |<sup>2</sup>E<sub>g</sub>⟩<sub>1</sub> and |<sup>2</sup>E<sub>g</sub>⟩<sub>2</sub>) 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.  $E[x \rightarrow y] |\Psi\rangle$  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 <sup>-1</sup>	nm	
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub> (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				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub> (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				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	$E[2nb_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.85	3.46	27 867	359	3.61e-2
	$E[nb_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.06				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	$E[b_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.49	3.63	29 265	342	1.65e-1
	$E[d_{xy}d_{x^2-y^2}b_{1u} \rightarrow d_{xz}d_{yz}e_g]  ^4B_{1g}\rangle$	0.32				
	$E[a_u \rightarrow e_g]  ^4B_{1g}\rangle$	0.05				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	$E[2nb_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.83	3.66	29 496	339	4.79e-1
	$E[nb_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.09				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	$E[nb_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.62	3.68	29 700	337	5.41e-2
	$E[b_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.13				
	$E[d_{xy}d_{z^2}b_{1u} \rightarrow d_{xz}d_{yz}e_g]  ^4B_{1g}\rangle$	0.11				
	$E[2nb_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.06				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	$E[d_{xy}d_{z^2}b_{1u} \rightarrow d_{xz}d_{yz}e_g]  ^4B_{1g}\rangle$	0.54	4.18	33 683	297	4.73e-2
	$E[b_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.33				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	$E[b_{1u} \rightarrow e_g]  ^4B_{1g}\rangle$	0.79	4.35	35 083	285	1.99e-2

Table SI14. Continuation

Transition	Excitation	weight*	Energy			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	E[d <sub>xy</sub> d <sub>z2</sub> b <sub>1u</sub> → d <sub>xz</sub> d <sub>yz</sub> e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.54	4.39	35 414	282	1.36e-2
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.33				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.74	4.45	35 909	278	1.28e-2
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.45	4.74	38 244	261	2.53e-1
	E[d <sub>xy</sub> d <sub>z2</sub> a <sub>u</sub> → d <sub>xz</sub> d <sub>yz</sub> e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.43				
<sup>4</sup> B <sub>1g</sub> → <sup>4</sup> E <sub>u</sub>	E[d <sub>z2</sub> d <sub>z2</sub> a <sub>u</sub> → d <sub>xz</sub> d <sub>yz</sub> e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.69	4.75	38 273	261	8.87e-3
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.09				
	E[d <sub>xy</sub> d <sub>xy</sub> a <sub>u</sub> → d <sub>xz</sub> d <sub>yz</sub> e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.06				
	E[d <sub>xy</sub> a <sub>u</sub> → d <sub>x2-y2</sub> e <sub>g</sub> ]   <sup>4</sup> B <sub>1g</sub> ⟩	0.05				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub> <sup>(a)</sup> (Q-band)	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.36	2.18	17 609	568	3.78e-2
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.26				
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.20				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.14				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub> (Q-band)	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.38	2.22	17 878	559	4.74e-2
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.24				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.20				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.12				



Table SI14. Continuation

Transition	Excitation	weight*	Energy			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.32	2.95	23 830	420	1.25
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.26				
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.16				
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.10				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.34	2.99	24 118	415	1.34
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.22				
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.20				
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.10				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.56	3.17	25 546	391	1.24e-2
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.28				
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.56	3.31	26 715	374	3.18e-2
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.26				
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.52	3.41	27 509	364	6.61e-2
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.26				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.10				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.46	3.63	29 297	341	1.58e-2
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.18				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.08				
	E[d <sub>z2</sub> b <sub>1u</sub> →d <sub>x2-y2</sub> e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.08				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.06				

Table SI14. Continuation

Transition	Excitation	weight*	Energy			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[2nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.54	3.63	29 313	341	2.19e-1
	E[2nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.26				
	E[nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.08				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[2nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.54	3.70	29 879	335	2.23e-1
	E[2nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.30				
	E[nb <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.06				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.62	4.31	34 740	288	2.50e-2
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.22				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> B <sub>1u</sub>	E[d <sub>xy</sub> a <sub>u</sub> → d <sub>x<sup>2</sup>-y<sup>2</sup></sub> e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.66	5.03	40 570	246	2.15e-2
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.12				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub> (Q-band)	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.38	2.19	17 642	567	5.04e-2
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.24				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.22				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.12				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub> (Q-band)	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.38	2.20	17 754	563	4.13e-2
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.24				
	E[a <sub>u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.22				
	E[b <sub>1u</sub> → e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.14				

Table SI14. Continuation

Transition	Excitation	weight*	Energy			<i>f</i>
			eV	cm <sup>-1</sup>	nm	
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.34	2.93	23 636	423	1.34
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.20				
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.18				
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.14				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub> (B-band)	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.36	3.01	24 307	411	1.35
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.20				
	E[b <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.18				
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.12				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.52	3.36	27 099	369	2.06e-2
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.34				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub>	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.52	3.42	27 574	363	3.43e-2
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.32				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.36	3.61	29 119	343	8.75e-3
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.30				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.48	3.67	29 598	338	2.27e-1
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.34				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.10				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub>	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.52	3.71	29 918	334	2.23e-1
	E[2nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	0.32				
	E[nb <sub>1u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.08				
<sup>4</sup> E <sub>g</sub> → <sup>4</sup> A <sub>u</sub>	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>1</sub>	0.62	4.42	35 632	281	5.67e-2
	E[a <sub>u</sub> →e <sub>g</sub> ]   <sup>4</sup> E <sub>g</sub> ⟩ <sub>2</sub>	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	<i>f</i>	Energy	<i>f</i>	Energy	<i>f</i>
${}^2E_g \rightarrow {}^2A_u$	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	<i>f</i>	Energy	<i>f</i>	Energy	<i>f</i>
${}^4B_{1g} \rightarrow {}^4E_u$	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	<i>f</i>	Energy	<i>f</i>	Energy	<i>f</i>
$^4E_g \rightarrow ^4A_u$	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		