Supplementary Information

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A Conversion factors

Dipole and rotational strengths were converted from atomic to CGS units with conversion factors taken from Ref. 1.

- 1 a.u. of dipole strength $(e^2 a_a^2) = 6.46048 \times 10^{-36} \text{ esu}^2 \text{ cm}^2$
- 1 a.u. of rotational strength $\left(\frac{e^2\hbar^2 a_o}{m_e}\right) = 4.71444 \times 10^{-38}$ esu cm erg G⁻¹

B Spin-Orbit Operator

Spin-orbit coupling constants describe the coupling between states of different spin-multiplicity. The spin-orbit coupling constant between a singlet state ${}^{1}m$ and a triplet state ${}^{3}n$ is given by $\langle {}^{1}m|V^{\rm SOC}|{}^{3}n\rangle$ where $V^{\rm SOC}$ is the spin-orbit operator. The calculations of these matrix elements are non-trivial². $V^{\rm SOC}$ affects both the spin and the spatial part of the wave function. The effective one-electron spin-orbit coupling operator can be expressed in the second quantisation representation³ in various equivalent ways, using e.g. Cartesian or spin-tensor components in different conventions:

$$V^{\text{SOC}} = \frac{1}{2} \sum_{pq} (V_{pq}^{x} T_{pq}^{x} + V_{pq}^{y} T_{pq}^{y} + V_{pq}^{z} T_{pq}^{z})$$
(1)

$$= \frac{1}{2} \sum_{pq} (V_{pq}^+ T_{pq}^{1,-1} - V_{pq}^- T_{pq}^{1,+1} + V_{pq}^z T_{pq}^z)$$
(2)

$$= \frac{1}{2} \sum_{pq} \left(-V_{pq}^{1,+1} T_{pq}^{1,-1} - V_{pq}^{1,-1} T_{pq}^{1,+1} + V_{pq}^{1,0} T_{pq}^{1,0} \right)$$
(3)

The Cartesian components of the triplet excitation operator are given by

$$T_{pq}^x = a_{p\alpha}^{\dagger} a_{q\beta} + a_{p\beta}^{\dagger} a_{q\alpha} \tag{4}$$

$$T_{pq}^y = \frac{1}{i} (a_{p\alpha}^{\dagger} a_{q\beta} - a_{p\beta}^{\dagger} a_{q\alpha})$$
(5)

$$T_{pq}^{z} = a_{p\alpha}^{\dagger}a_{q\alpha} - a_{p\beta}^{\dagger}a_{q\beta} \tag{6}$$

The prefactor 1/2 in the Cartesian triplet operators has been moved in front of the summation in the expression for V^{SOC} . Otherwise, these equations directly compare with the equations in Ref. 3.

The three components of the triplet excitation operator in spin tensor form are given by:

$$T_{pq}^{1,-1} = a_{p\beta}^{\dagger} a_{q\alpha} , \qquad (7)$$

$$T_{pq}^{1,+1} = -a_{p\alpha}^{\dagger}a_{q\beta} , \qquad (8)$$

$$T^{1,0}_{pq} = \frac{1}{\sqrt{2}} (a^{\dagger}_{p\alpha} a_{q\alpha} - a^{\dagger}_{p\beta} a_{q\beta}) .$$

$$\tag{9}$$

The relations between the Cartesian and the spin tensor form of the triplet excitation operators are:

$$T_{pq}^x = -T_{pq}^{1,+1} + T_{pq}^{1,-1} , \qquad (10)$$

$$T_{pq}^{y} = \frac{1}{i} \left(-T_{pq}^{1,+1} - T_{pq}^{1,-1} \right) , \qquad (11)$$

$$T_{pq}^{z} = T_{pq} = \sqrt{2}T_{pq}^{1,0} .$$
 (12)

The transformation matrix elements between the Cartesian and the spin tensor forms can then be obtained from the definition of the triplet excitation operators in these forms. V^{SOC} can be written as:

$$V^{\text{SOC}} = \frac{1}{2} \sum_{pq} \left(V_{pq}^{x} (-T_{pq}^{1,+1} + T_{pq}^{1,-1}) + V_{pq}^{y} \frac{1}{i} (-T_{pq}^{1,+1} - T_{pq}^{1,-1}) \right)$$
(13)

$$+V_{pq}^{z}\sqrt{2}T_{pq}^{1,0}\right) = \frac{1}{2}\sum_{pq}\left((V_{pq}^{x}+iV_{pq}^{y})T_{pq}^{1,-1}-(V_{pq}^{x}-iV_{pq}^{y})T_{pq}^{1,+1}+\sqrt{2}V_{pq}^{z}T_{pq}^{1,0}\right) \quad (14)$$

This leads to the following identities:

$$V_{pq}^{1,-1} = -(V_{pq}^x + iV_{pq}^y) = -V_{pq}^+ , \qquad (15)$$

$$V_{pq}^{1,+1} = -(V_{pq}^x - iV_{pq}^y) = -V_{pq}^- , \qquad (16)$$

$$V_{pq}^{1,0} = \sqrt{2}V_{pq}^z . (17)$$

B.1 Matrix Elements of the Spin-Orbit Operator

If the reference states are closed-shell, spin symmetry can be utilised to introduce singlet- and triplet-adapted excitation operators. Both, the Hamiltonian and the components of the dipole operator, can be expressed in a spin-free form⁴. For spin-forbidden transitions involving a singlet and a triplet state, the three components of the triplet state can couple to the singlet state through the three components of the SOC operator:

$$\langle {}^{1}0|V^{\text{SOC}}|^{3,M_{S}}f\rangle = \begin{cases} -\frac{1}{2}\sum_{pq}V_{pq}^{1,+1}\langle {}^{1}0|T_{pq}^{1,-1}|^{3,+1}f\rangle \\ -\frac{1}{2}\sum_{pq}V_{pq}^{1,-1}\langle {}^{1}0|T_{pq}^{1,+1}|^{3,-1}f\rangle \\ +\frac{1}{2}\sum_{pq}V_{pq}^{1,0}\langle {}^{1}0|T_{pq}^{1,0}|^{3,0}f\rangle \end{cases}$$
(18)

The $M_S = 0$ component $(T_{pq}^z = T_{pq}^{1,0})$ does not change the M_S quantum number. A formulation that requires only the $\langle {}^10|T_{pq}|^{3,0}f\rangle$ matrix element of the T_{pq} operator can be found using the Wigner-Eckart theorem. This allows the treatment of singlet-triplet transitions in a spin-free formalism without generating the $M_S = +1$ and $M_S = -1$ components of the triplet state.

B.2 Wigner-Eckart Theorem

The Wigner-Eckart theorem⁵ (WET) can be applied to generate equalities where all components of the triplet state are expressed using only the $\langle {}^{1}0|T_{pq}|^{3,0}f\rangle$ matrix element of the T_{pq} operator. With the help of the WET

$$\langle j'm'''|T^{kq'}|jm''\rangle = (-1)^{m'''-m'} \frac{\begin{pmatrix} j' & k & j \\ -m''' & q' & m'' \end{pmatrix}}{\begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix}} \langle j'm'|T^{kq}|jm\rangle$$
(19)

In our case, j' = 0, m''' = m' = 0, k = j = 1. We thus need the 3j symbols $\begin{pmatrix} 0 & 1 & 1 \\ 0 & q & m \end{pmatrix}$. The values are 0 for $q \neq -m$, so that we are left with the 3j symbols $\begin{pmatrix} 0 & 1 & 1 \\ 0 & -m & m \end{pmatrix}$ which are $1/\sqrt{3}$ for m = -1, +1 and $-1/\sqrt{3}$ for m = 0. This leads to the following equalities:

$$\langle {}^{1}0|T^{1,0}_{pq}|^{3,0}f\rangle = \frac{1}{\sqrt{2}}\langle {}^{1}0|T_{pq}|^{3,0}f\rangle$$
(20)

$$\langle {}^{1}0|T^{1,-1}_{pq}|^{3,+1}f\rangle = -\langle {}^{1}0|T^{1,0}_{pq}|^{3,0}f\rangle = -\frac{1}{\sqrt{2}}\langle {}^{1}0|T_{pq}|^{3,0}f\rangle$$
(21)

$$\langle {}^{1}0|T_{pq}^{1,+1}|^{3,-1}f\rangle = -\langle {}^{1}0|T_{pq}^{1,0}|^{3,0}f\rangle = -\frac{1}{\sqrt{2}}\langle {}^{1}0|T_{pq}|^{3,0}f\rangle$$
(22)

The matrix elements of the SOC operator can then be expressed as

$$\langle {}^{1}0|V^{\rm SOC}|^{3,+1}f\rangle = \frac{1}{2}\sum_{pq}V^{1,+1}_{pq}\langle {}^{1}0|T_{pq}|^{3,0}f\rangle$$
(23)

$$\langle {}^{1}0|V^{\text{SOC}}|^{3,-1}f\rangle = \frac{1}{2}\sum_{pq}V^{1,-1}_{pq}\langle {}^{1}0|T_{pq}|^{3,0}f\rangle$$
(24)

$$\langle {}^{1}0|V^{\rm SOC}|{}^{3,0}f\rangle = \frac{1}{2}\sum_{pq}V^{1,0}_{pq}\langle {}^{1}0|T_{pq}|{}^{3,0}f\rangle$$
(25)

B.3 Phosphorescence

The spin-forbidden emission, e.g. from an excited triplet state $|{}^{3}f\rangle$ to a singlet ground state $|{}^{1}0\rangle$, are called phosphorescence. To compute oscillator strengths for phosphorescence, the first-order transition dipole matrix elements between the initial and final states accumulated over the three M_{S} components are required. For exact spin eigen functions, the dipole transition moment vanishes for states of different multiplicities. But when spin-orbit interactions are considered the eigenfunctions of the electronic Hamiltonian are no longer pure spin states⁶. The first non-vanishing SOC correction to the dipole transition strength is:

$$\sum_{m} |\langle^{1}0|\mathbf{r}|^{3,m}f\rangle^{(1)}|^{2} = \sum_{m} \left(\langle^{3,m}f|x|^{1}0\rangle^{(1)}\langle^{1}0|x|^{3,m}f\rangle^{(1)}\right)$$
(26)

$$+ \langle^{3,m} f | y | {}^{1} 0 \rangle^{(1)} \langle^{1} 0 | y | {}^{3,m} f \rangle^{(1)}$$

$$+ \langle^{3,m} f | z | {}^{1} 0 \rangle^{(1)} \langle^{1} 0 | z | {}^{3,m} f \rangle^{(1)})$$
(27)

Using perturbation theory, the spin contaminants can be expanded in a set of intermediate states to obtain a sum-over-states (SOS) expression for exact states:

$$\langle {}^{1}0|x|^{3,m}f\rangle^{(1)} = \sum_{\substack{1_k}} \frac{\langle {}^{1}0|x|^{1}k\rangle\langle {}^{1}k|V^{\text{SOC}}|^{3,m}f\rangle}{\omega_f - \omega_k} , \qquad (28)$$
$$-\sum_{\substack{3,m_k}} \frac{\langle {}^{1}0|V^{\text{SOC}}|^{3,m}k\rangle\langle {}^{3,m}k|x|^{3,m}f\rangle}{\omega_k} .$$

For the unperturbed states, the excitation energies ω_k for the three components of a triplet intermediate state ³k do not depend on m.

We can rewrite the last equation as

$$\langle {}^{1}0|x|^{3,m}f\rangle^{(1)} = \langle {}^{1}\tilde{0}_{x}|V^{\text{SOC}}|^{3,m}f\rangle + \langle {}^{1}0|V^{\text{SOC}}|^{3,m}\tilde{f}_{x}\rangle$$
(29)

with the short-hand notation

$$|^{1}\tilde{0}_{x}\rangle = \sum_{k} |^{1}k\rangle \frac{\langle k|x|^{1}0\rangle}{\omega_{f} - \omega_{k}}$$
(30)

$$|^{3,m}\tilde{f}_x\rangle = \sum_{3,mk} |^{3,m}k\rangle \frac{\langle^{3,m}k|x|^{3,m}f\rangle}{-\omega_k}$$
(31)

We can then express the first-order transition strengths as

$$\langle^{3,m}f|x|^{1}0\rangle^{(1)}\langle^{1}0|x|^{3,m}f\rangle^{(1)} =$$

$$\sum_{m} \left(\langle^{1}\tilde{0}_{x}|V^{\text{SOC}}|^{3,m}f\rangle + \langle^{1}0|V^{\text{SOC}}|^{3,m}\tilde{f}_{x}\rangle \right)^{*} \times \left(\langle^{1}\tilde{0}_{x}|V^{\text{SOC}}|^{3,m}f\rangle + \langle^{1}0|V^{\text{SOC}}|^{3,m}\tilde{f}_{x}\rangle \right)$$
(32)

Four contributions are obtained on opening the parentheses, all of the form:

$$\sum_{m} \langle {}^{1}i|V^{\text{SOC}}|^{3,m}f \rangle^{*} \langle {}^{1}j|V^{\text{SOC}}|^{3,m}g \rangle$$

$$= \frac{1}{4} \sum_{pq,rs} \left(\langle {}^{1}i|V_{pq}^{1,+1}T_{pq}^{1,-1}|^{3,+1}f \rangle^{*} \langle {}^{1}j|V_{rs}^{1,+1}T_{rs}^{1,-1}|^{3,+1}g \rangle \right.$$

$$+ \langle {}^{1}i|V_{pq}^{1,-1}T_{pq}^{1,+1}|^{3,-1}f \rangle^{*} \langle {}^{1}j|V_{rs}^{1,-1}T_{rs}^{1,+1}|^{3,-1}g \rangle$$

$$+ \langle {}^{1}i|V_{pq}^{1,0}T_{pq}^{1,0}|^{3,0}f \rangle^{*} \langle {}^{1}j|V_{rs}^{1,0}T_{rs}^{1,0}|^{3,0}g \rangle \right)$$

$$(33)$$

$$= \frac{1}{4} \sum_{pq,rs} \left((V_{pq}^{1,+1})^* V_{rs}^{1,+1} + (V_{pq}^{1,-1})^* V_{rs}^{1,-1} + (V_{pq}^{1,0})^* V_{rs}^{1,0} \right)$$
(34)

$$\times \langle {}^{1}i|T_{pq}^{1,0}|^{3,0}f \rangle^{*} \langle {}^{1}j|T_{rs}^{1,0}|^{3,0}g \rangle$$

$$= \frac{1}{4} \sum \left((V_{pq}^{x} + iV_{pq}^{y})^{*} (V_{rs}^{x} + iV_{rs}^{y}) + (V_{pq}^{x} - iV_{pq}^{y})^{*} (V_{rs}^{x} - iV_{rs}^{y}) \right)$$

$$(35)$$

$$= \frac{1}{4} \sum_{pq,rs} \left((V_{pq}^x + iV_{pq}^y)^* (V_{rs}^x + iV_{rs}^y) + (V_{pq}^x - iV_{pq}^y)^* (V_{rs}^x - iV_{rs}^y) + \sqrt{2} (V_{pq}^z)^* \sqrt{2} V_{rs}^z \right) \times \langle {}^1i | \frac{1}{\sqrt{2}} T_{pq} | {}^{3,0}f \rangle^* \langle {}^1j | \frac{1}{\sqrt{2}} T_{rs} | {}^{3,0}g \rangle$$
(35)

We get:

$$\begin{split} \sum_{m} \langle {}^{1}i|V^{\text{SOC}}|^{3,m}f \rangle^{*} \langle {}^{1}j|V^{\text{SOC}}|^{3,m}g \rangle \\ &= \frac{1}{4} \sum_{pq,rs} \left(2(V_{pq}^{x})^{*}V_{rs}^{x} + 2(V_{pq}^{y})^{*}V_{rs}^{y} + 2(V_{pq}^{z})^{*}V_{rs}^{z} \right) \quad (36) \\ &\qquad \times \frac{1}{2} \langle {}^{1}i|T_{pq}|^{3,0}f \rangle^{*} \langle {}^{1}j|T_{rs}|^{3,0}g \rangle \\ &= \frac{1}{4} \sum_{\alpha=x,y,z} \langle {}^{1}i|\sum_{pq} V_{pq}^{\alpha}T_{pq}|^{3,0}f \rangle^{*} \langle {}^{1}j|\sum_{rs} V_{rs}^{\alpha}T_{rs}|^{3,0}g \rangle \quad (37) \\ &= \sum_{\alpha=x,y,z} \langle {}^{1}i|\frac{1}{2} \sum_{pq} V_{pq}^{\alpha}T_{pq}|^{3,0}f \rangle^{*} \langle {}^{1}j|\frac{1}{2} \sum_{rs} V_{rs}^{\alpha}T_{rs}|^{3,0}g \rangle \quad (38) \end{split}$$

Here, i and j are the perturbed or unperturbed singlet state. Similarly, f and g are the perturbed or unperturbed triplet state.

B.4 Generalisation to Circularly Polarised Phosphorescence

The derivation in the last section exploited only the facts that

- the formula for the transition strength includes a summation over the m components of the triplet state and
- the transition operators do not affect the spin.

The result is also valid if x as transition operator in the left or the right transition moment is replaced by other operators which do not effect the spin as e.g. components of the electronic momentum \mathbf{p} or the electronic angular momentum \mathbf{L} , which is appears in the operator for the magnetic field. As long as this precondition is fulfilled for two operators X and Y we can write the transition strength accumulated over the three M_S components of the triplet state as:

$$\sum_{m=} \langle {}^{1}0|X|^{3}f \rangle {}^{(1)} \langle {}^{3}f|Y|^{1}0 \rangle {}^{(1)} = \sum_{\alpha=x,y,z} T_{0f}^{X,\alpha} T_{f0}^{Y,\alpha}$$
(39)

where

$$T_{0f}^{X,\alpha} = \sum_{k} \frac{\langle {}^{1}0|X|^{1}k \rangle \langle {}^{1}k|\frac{1}{2} \sum_{pq} V_{pq}^{\alpha} T_{pq}|^{3,0} f \rangle}{\omega_{f} - \omega_{k}} , \qquad (40)$$
$$- \sum_{3,0k} \frac{\langle {}^{1}0|\frac{1}{2} \sum_{pq} V_{pq}^{\alpha} T_{pq}|^{3,0}k \rangle \langle {}^{3,0}k|X|^{3,0} f \rangle}{\omega_{k}} ,$$

is evaluated with the $M_S = 0$ components of the triplet states.

The rotational strength tensor is written as a sum of an electric dipoleelectric quadrupole contribution and an electric dipole-magnetic dipole contribution^{7,8}. The pseudoscalar rotational strength for isotropic samples is obtained by orientational averaging of the rotational strength tensor and thereby the contribution from the quadrupole moment vanishes. To compute the pseudoscalar rotational strengths for circularly polarised phosphorescence of an isotropic sample, the first-order transition dipole matrix elements between the initial and final states averaged over the M_S components are required. This is similar to phosphorescence. But now for the velocity gauge formulation, we need transition matrix elements for the linear and angular momentum operators:

$$\langle {}^{1}0|\mathbf{p}|{}^{3}f\rangle\langle {}^{3}f|\mathbf{L}|{}^{1}0\rangle = \sum_{\beta=x,y,z}\sum_{\alpha=x,y,z}T_{0f}^{p_{\beta},\alpha}T_{f0}^{L_{\beta},\alpha}$$
(41)

B.5 Dipole strength in velocity gauge

For the dipole strengths, the results are similar to oscillator strengths, the differ only in a scalar factor. The results for the dipole strength in the length gauge were already given in Sec. B.3. The first non-vanishing SOC correction to the dipole strength in the velocity gauge formulation is:

$$\sum_{m} |\langle^{1}0|\mathbf{p}|^{3,m}f\rangle^{(1)}|^{2} = \langle^{1}0|\mathbf{p}|^{3}f\rangle\langle^{3}f|\mathbf{p}|^{1}0\rangle = \sum_{\beta=x,y,z} \sum_{\alpha=x,y,z} T_{0f}^{p_{\beta},\alpha} T_{f0}^{p_{\beta},\alpha} \quad (42)$$

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