Supporting Information

for

Theoretical studies on the absorption spectra of *cis*-[Ru(4,4'-COO-2,2'-bpy)$_2$(X)$_2$]$^{4-}$, (X = NCS, Cl) in water and panchromatic trans-terpyridyl Ru complexes in methanol solution based on time-dependent density functional theory including strong spin-orbit couplings

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Theory: First-order perturbation theory for molecules having strong SO couplings

The theory of absorption spectra for molecules having strong SO coupling has been developed by Nozaki [S1]. It is based on the first-order perturbation theory of SO coupling matrix elements. For the Ru complexes in mind, the first-order perturbation theory is accurate enough, because the largest one electron spin-orbit coupling constant for Ru atom in the $(4d)^6$ configuration (1081 cm^{-1} ~ 0.13 eV) is only about 10 % of the first electronic excitation energy. In order for the present paper to be self-contained, we will briefly introduce the theory and point out some missing formulas in the original theory [S1].

From the degenerate perturbation theory, the k-th molecular wavefunction perturbed by SO coupling, $\left|\Psi_k^{SO}\right\rangle$, is given by

$$\left|\Psi_k^{SO}\right\rangle = \sum_{\substack{\sigma=S,T \\ i}} c_{k,i}^\sigma \left|\Psi_i'^\sigma\right\rangle \tag{S1}$$

where σ is the spin index, S and T stand for singlet and triplet states, respectively, $\left|\Psi_i'^\sigma\right\rangle$ is the i-th unperturbed wavefunction of the molecule, and $c_{k,i}^\sigma$ is the coefficient of the linear combination of the perturbed molecular wavefunction. From the general perturbation theory for degenerate quantum states, the perturbation energy due to SO coupling, E_{SO}, is expressed as

$$\left(\left\langle\Psi'\right|\hat{H}_{SO}\left|\Psi'\right\rangle - E_{SO}I\right)C = 0, \tag{S2}$$

where $\hat{H}_{SO}$ is the SO coupling Hamiltonian, $\boldsymbol{I}$ is the unit matrix, and $\boldsymbol{C}$ is the coefficient column vector for $c_{k,i}^\sigma$. As shown in FigS1., under the assumption of the ground-state electronic wavefunction, $\left|\Phi_g^\sigma\right\rangle$, consisting of a single determinant of Kohn-Sham orbitals with spin index σ, we can approximate the k-th unperturbed

molecular excited-state electronic wavefunction, $\left|\Psi_k'^{\sigma}\right\rangle$, as a linear combination of one-electron excitation configurations from the *p*-th molecular orbital (MO) with spin σ (ϕ_p^{σ}) to the *q*-th MO with spin σ (ϕ_q^{σ}), $\left|\Phi_k^{\sigma}(p \to q)\right\rangle$:

$$\left|\Psi_k'^{\sigma}\right\rangle = \sum_{p=1}^{occ} \sum_{q=occ+1} a_{pqk}^{\sigma} \left|\Phi_k^{\sigma}(p \to q)\right\rangle, \tag{S3}$$

where a_{pqk}^{σ} is the coefficient of the linear combination of the unperturbed molecular excited-state electronic wavefunction in terms of $\left|\Phi_k^{\sigma}(p \to q)\right\rangle$.

The SO coupling matrix elements between the *k*-th and the *l*-th unperturbed wavefunctions, $\left\langle \Psi_k'^{\sigma} \left| \hat{H}_{SO} \right| \Psi_l'^{\sigma'} \right\rangle$, can be approximately represented by the sum of one-electron one-center SO integrals between these electronic configurations, as shown in FigS2. [S2, S3]:

$$\left\langle \Psi_k'^{\sigma} \left| \hat{H}_{SO} \right| \Psi_l'^{\sigma'} \right\rangle = \sum_{p=1}^{occ} \sum_{q=occ+1} \sum_{r=occ+1} a_{pqk}^{\sigma} a_{prl}^{\sigma'} \left\langle \Phi_k^{\sigma}(p \to q) \left| \hat{H}_{SO} \right| \Phi_l^{\sigma'}(p \to r) \right\rangle$$

$$+ \sum_{q=occ+1} \sum_{p=1}^{occ} \sum_{r=1}^{occ} a_{pqk}^{\sigma} a_{rql}^{\sigma'} \left\langle \Phi_k^{\sigma}(p \to q) \left| \hat{H}_{SO} \right| \Phi_l^{\sigma'}(r \to q) \right\rangle. \tag{S4}$$

To evaluate one-electron one-center SO integrals presented in FigS2. ((a) is for singlet transition and (b) is for triplet transition), we will use natural atomic orbitals ($\left|\chi_j\right\rangle$, NAO) to expand molecular orbitals:

$$\left|\phi\right\rangle = \sum_j b_j \left|\chi_j\right\rangle, \tag{S5}$$

where $|\phi\rangle$ is the atomic orbital (AO) and b_j is the coefficient of the representation of the linear combination of AO, $|\phi\rangle$, in terms of NAO's, $|\chi_j\rangle$. Here, Kohn-Sham ground state, $|\Phi_g^\sigma\rangle$, can be expressed as

$$\left|\Phi_g^\sigma\right\rangle = \frac{1}{\sqrt{N!}} \left|\phi_1 \, \mathsf{L} \, \phi_N\right|, \tag{S6}$$

where $|\mathsf{L}|$ denotes the Slater determinant. NAO's are optimal (maximum occupancy) effective AO's in the molecular environment. The use of NAO's is very advantageous compared with that of other types of AO's. For example, NAO's allow us to avoid the basis set dependence of calculation results because one specific NAO is localized one-center orbital that maintains intra- and inter-atomic orthogonality to the remaining NAO's. Using NAO's, the SO integral, $\left\langle \Psi_k'^\sigma \left| \hat{H}_{SO} \right| \Psi_l'^{\sigma'} \right\rangle$, can be evaluated as

$$\left\langle \Psi_k'^\sigma \left| \hat{H}_{SO} \right| \Psi_l'^{\sigma'} \right\rangle = \sum_{p=1}^{occ} \sum_{q=occ+1} \sum_{r=occ+1} a_{pqk}^\sigma a_{prl}^{\sigma'} \sum_m \sum_n b_{qm} b_{rn} \Xi_{mn}^{\sigma\sigma'}(v)$$

$$+ \sum_{q=occ+1} \sum_{p=1}^{occ} \sum_{r=1}^{occ} a_{pqk}^\sigma a_{rql}^{\sigma'} \sum_m \sum_n b_{pm} b_{rn} \Xi_{mn}^{\sigma\sigma'}(o). \tag{S7}$$

Here, for example,

$$\Xi_{mn}^{\sigma\sigma'}(v) = \frac{1}{2} \left(\left\langle \chi_{d_{xy}}^\alpha \left| \hat{H}_{SO} \right| \chi_{d_{xz}}^\beta \right\rangle + \left\langle \chi_{d_{xy}}^\beta \left| \hat{H}_{SO} \right| \chi_{d_{xz}}^\alpha \right\rangle \right), \tag{S8}$$

if the valence orbital contributing to the SO integrals is d-orbital. Owing to the fact that NAO's with the intra-atomic orthogonality are similar to the Slater orbitals in shape, for example, the SO integral in terms of NAO's given in Eq. (S8), $\left\langle \chi_{d_{xy}}^\alpha \left| \hat{H}_{SO} \right| \chi_{d_{xz}}^\beta \right\rangle$, can be approximated by the SO integral between the corresponding Slator orbitals,

$$\left\langle \chi_{d_{xy}}^\alpha \left| \hat{H}_{SO} \right| \chi_{d_{xz}}^\beta \right\rangle \sim \zeta_c \left\langle \chi_{d_{xy}}^\alpha \left| \hat{H}_{SO} \right| \chi_{d_{xz}}^\beta \right\rangle = \frac{1}{2} \zeta_c, \tag{S9}$$

where ζ_c is the on-electron SO coupling constant for an effective SO potential resulting from the screening effect of the nuclear charge by the closed shell electrons [S4 – S8]. The values of ζ_c are given in [S4].

By solving the eigenvalue problem of Eq. (S2), one obtains the k-th molecular wavefunction perturbed by SO coupling, $\left|\Psi_k^{SO}\right\rangle$, given by Eq. (S1). Using the perturbed wavefunctions, the oscillator strength proportional to the strength of the absorption spectra, f, is given by

$$f = \frac{8\pi^2 m_e}{3he^2}\tilde{\nu}_{em}\left|\left\langle\Psi_g\left|\vec{\mu}\right|\Psi_k^{SO}\right\rangle\right|^2 = \frac{8\pi^2 m_e}{3he^2}\tilde{\nu}_{em}\left|\sum_{\substack{\sigma=S,T \\ i}} c_{k,i}^{\sigma}\left\langle\Psi_g\left|\vec{\mu}\right|\Psi_i'^{\sigma}\right\rangle\right|^2 , \quad (S10)$$

where m_e is the mass of the electron, h is the Planck's constant, e is the unit charge, $\vec{\mu}$ is the transition dipole moment operator, $\tilde{\nu}_{em}$ is the wavenumber of the incident electromagnetic wave, and $\left|\Psi_g\right\rangle$ is the ground-state electronic molecular wavefunction. The transition energy perturbed by the SO coupling, E_k^{new}, is given by the ordinary first-order perturbation theory:

$$E_k^{new} = E_k^{(0)} + E_{k,SO}^{(1)}, \quad\quad\quad\quad (S11)$$

where $E_k^{(0)}$ is the zero-th order energy and $E_{k,SO}^{(1)}$ is the first-order perturbation energy calculated by Eq. (S2).
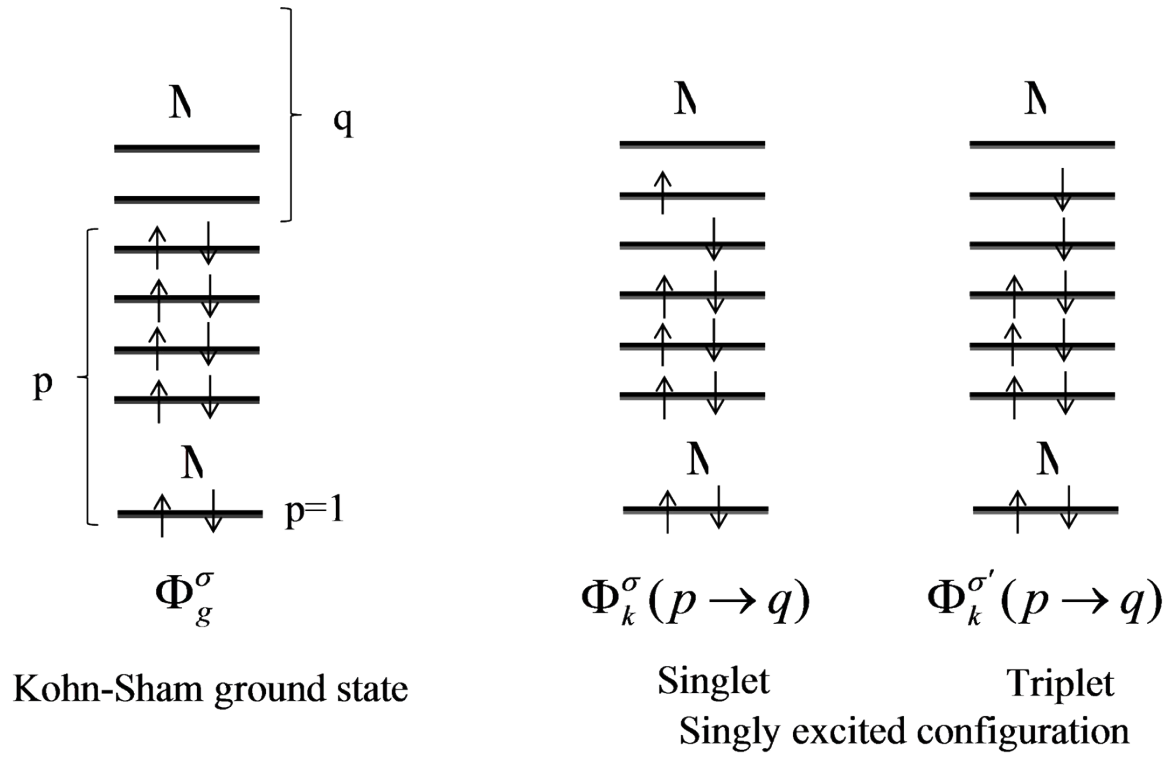
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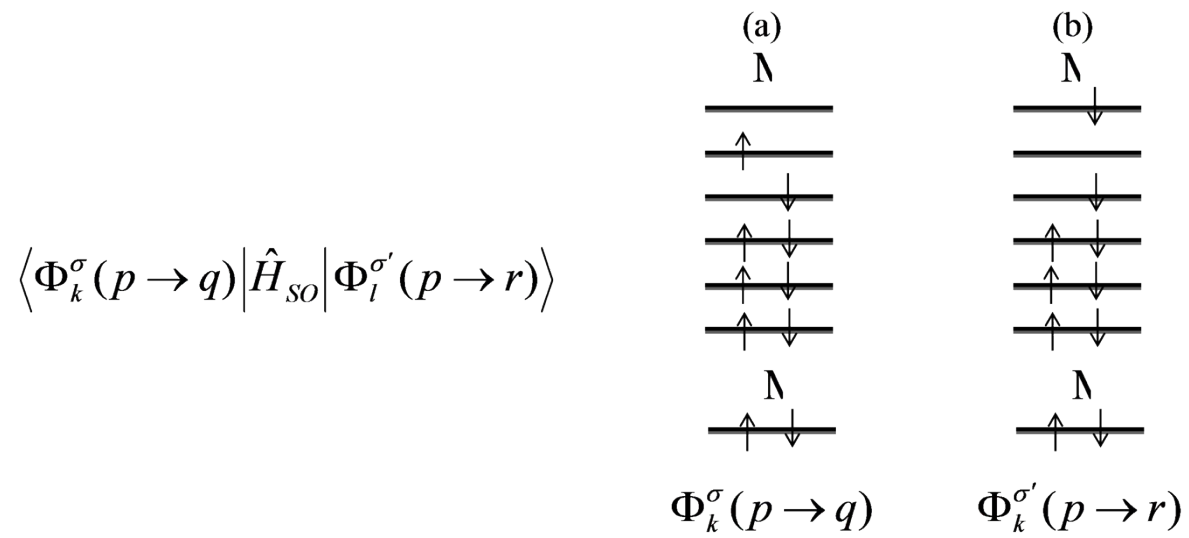
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Figure Captions for Supporting Information

FigS1. Pictorial representations of Kohn-Sham molecular ground state with spin index σ $\left|\Phi_g^\sigma\right\rangle$ (usually, because the ground state is the singlet state, $\sigma = S$), and singly excited configurations to singlet ($\left|\Phi_k^\sigma(p \to q)\right\rangle$) and triplet states ($\left|\Phi_k^{\sigma'}(p \to q)\right\rangle$).

FigS2. Pictorial representation of the one-electron one-center SO integral, $\left\langle \Phi_k^\sigma(p \to q) \right| \hat{H}_{SO} \left| \Phi_l^{\sigma'}(p \to r) \right\rangle$, between the electronic configurations, $\Phi_k^\sigma(p \to q)$ and $\Phi_k^{\sigma'}(p \to r)$.

$$\Phi_g^\sigma \qquad \Phi_k^\sigma(p \to q) \qquad \Phi_k^{\sigma'}(p \to q)$$

Kohn-Sham ground state   Singlet   Triplet

Singly excited configuration

FigS1. K. Mishima *et al.*

$$\left\langle \Phi_k^{\sigma}(p \to q) \middle| \hat{H}_{SO} \middle| \Phi_l^{\sigma'}(p \to r) \right\rangle$$

(a)

(b)

$$\Phi_k^{\sigma}(p \to q)$$

$$\Phi_k^{\sigma'}(p \to r)$$

FigS2. K. Mishima *et al*.