Spin-Orbit coupling in p-methoxyphenyl-pyranoflavylium cation

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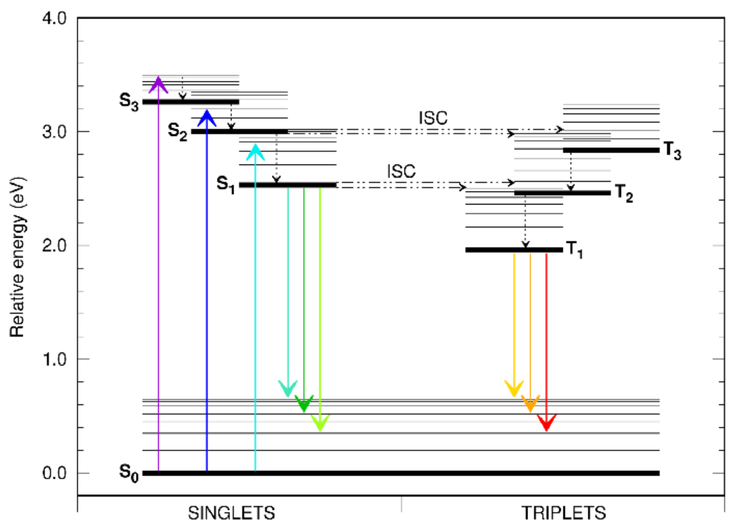
INTRODUCTION

Light emission from triplet excited states is enabled by intersystem crossing (ISC), which is briefly described as a spin multiplicity exchange. The transition from a singlet excited to a triplet excited state is forbidden, but the spin-orbit coupling (SOC) makes it feasible.[1]

The ISC efficiency and rate depend on SOC, which is sensible to different conformational arrangements. So, the spin-orbit coupling was calculated[2] as a function of the torsion dihedral angles of p-methoxyphenyl-pyranoflavylium[3] defined by the C-B rings and D-E rings.

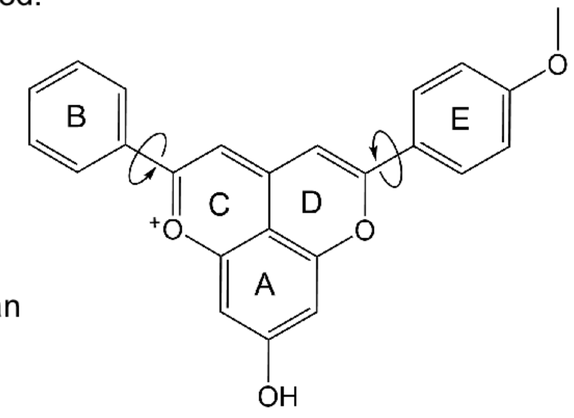


COMPUTATIONAL DETAILS

→ Time Dependent Density Functional Method:
B3LYP/D3BJ/6-311G(d,p)

→ Solvation Model:
C-PCM (acetonitrile)

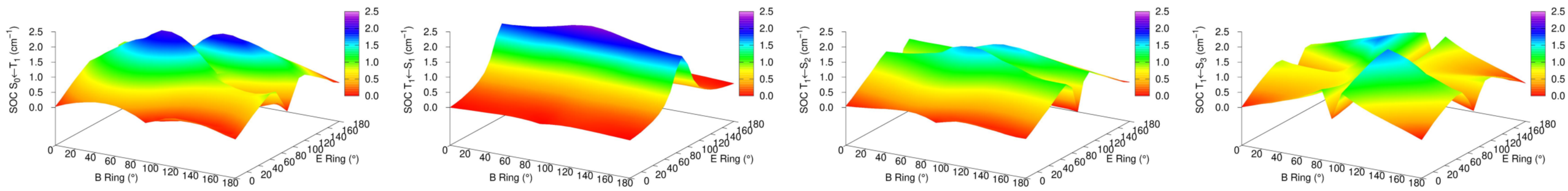
→ SOC Surfaces:
B and E-ring dihedral angles relaxed scan

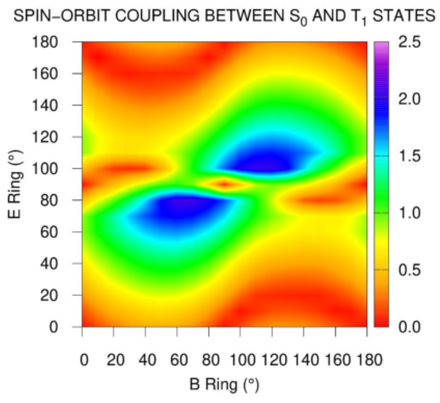


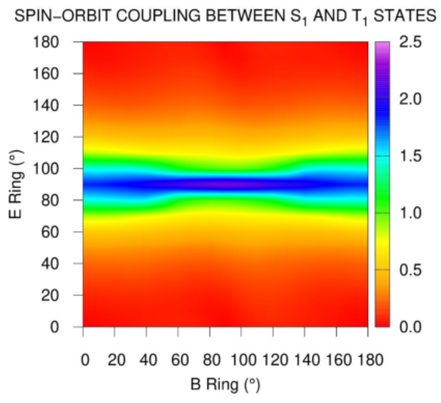
→ Spin-Orbit Coupling Calculations[2]:

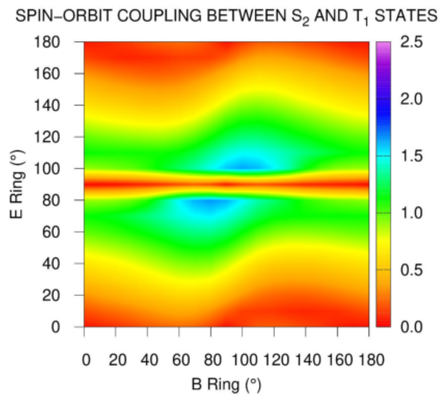
$$\hat{H}_{\mathrm{SOC}} = \sum_{m}^{0,\pm1} \sum_{pq} (-1)^m \, z_{pq}^{(-m)} \hat{S}_{pq}^{(m)} \qquad |\Psi_{\mathrm{SOC}}^{I}\rangle = C_0^I|0\rangle + \sum_{n}^{N_S} C_n^I|S_n\rangle + \sum_{M}^{0,\pm1} \sum_{k}^{N_T} C_{k,M}^I|T_k^M\rangle$$

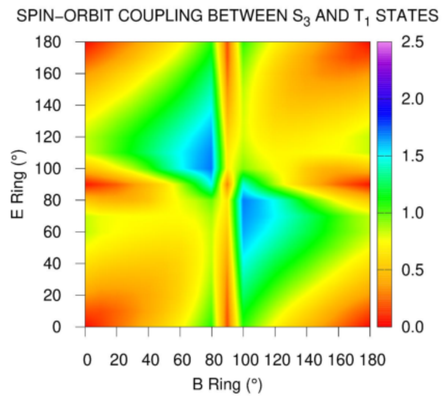
RESULTS

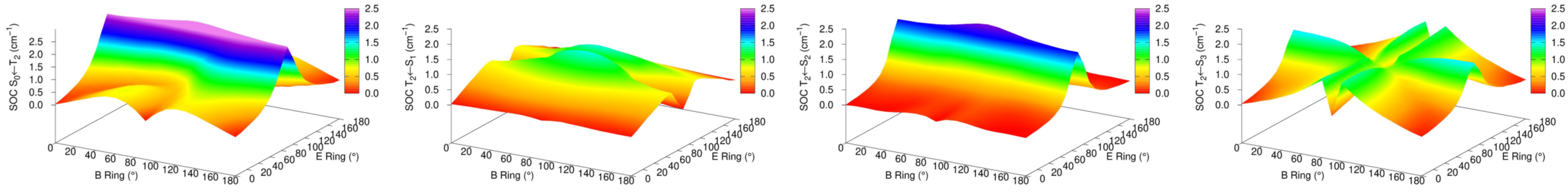


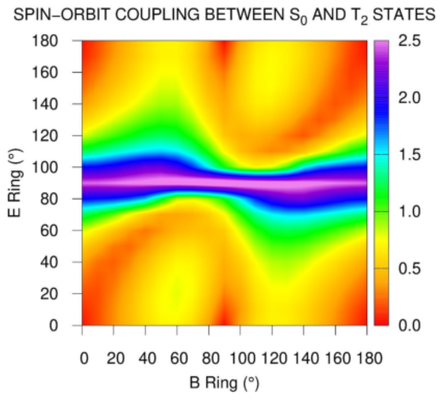


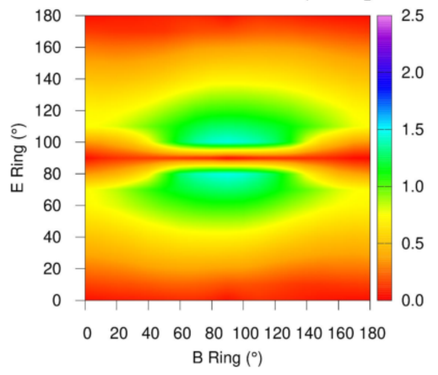


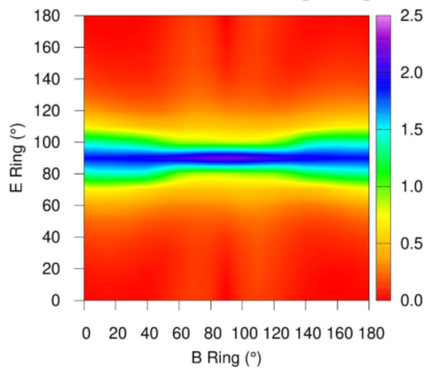


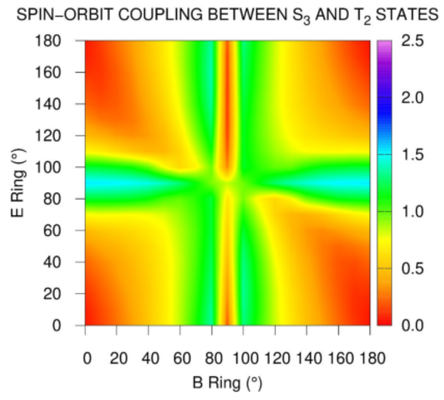












→ SOC (and ISC) is possible for all cases evaluated

→ Greater influence of the E-ring dihedral angles close to 90°

→ Planar conformations show up lower (close to zero) coupling values

→ Surfaces' symmetry reflects the rings' symmetry, mainly the B-ring

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