振電相互作用理論に基づくルブレンの吸収・蛍光スペクトルおよび輻射・無輻射速度定数の計算と解析

（MOLFEX[1]・京大福井セ[2]・京大院工[3]）○上島 基之[1]・福永 宏雄[1]・大田 航[2,3]・佐藤 徹[2,3]

Calculation and analysis of absorption and fluorescence spectra, and radiative and non-radiative rate constants of rubrene based on the theory of vibronic coupling

([1]*MOLFEX, Inc.*, [2]*Fukui Institute for Fundamental Chemistry, Kyoto University*, [3]*Graduate School of Engineering, Kyoto University,*) ○Motoyuki Uejima[1], Hiroo Fukuanaga[1], Wataru Ota,[2,3] Tohru Sato[2,3]

The vibronic coupling (VC) between the electronic and vibrational states, provides complex electronic spectral shapes due to the vibronic progressions, and induces non-radiative transitions. In particular, in the spin-mixed crude adiabatic (SMCA) representation, the non-radiative transition can be regarded as a one-phonon emission/absorption process driven by the VC, and the internal conversion and intersystem crossing can be treated in a unified manner. The normal modes can be classified into the promoting mode, which is involved in phonon emission/absorption, and the accepting mode, which receives the electron excitation energy. The origin of the VC can be analyzed by the vibronic coupling density, which facilitates the design of finely tuned molecules with respect to the spectral shape and non-radiative transitions.

In this study, we have calculated the absorption and fluorescence spectra of rubrene, and the radiative and non-radiative rate constants in the framework of SMCA picture, and compared them with the experiments. The vibrational modes that greatly contribute to the vibronic progressions and non-radiative transitions were assigned. The origin of the VCs was analyzed using the vibronic coupling density.

Keywords： Internal Conversion; Intersystem Crossing; Vibronic Coupling

電子状態と振動状態との間の相互作用である振電相互作用は振電プログレッションを与え、電子遷移スペクトルに複雑なスペクトル形状をもたらす[1)]。また振電相互作用は無輻射遷移の駆動力でもある。特に混合スピン粗断熱表現において無輻射遷移は振電相互作用を介した一フォノン放出、吸収過程とみなせ、内部転換と系間交差を統一的に扱うことができる[2)]。これらの振動モードにおける振電相互作用の起源は振電相互作用密度[3)]により解析でき、さらにはスペクトル形状や無輻射遷移を制御した分子設計への応用を可能にする。

本研究では混合スピン粗断熱描像に基づいてルブレンの吸収・蛍光スペクトルおよび輻射・無輻射遷移の速度定数を計算し、実測との比較を行った。振電プログレッションや無輻射遷移に寄与する主要な振動モードの帰属を行い、その振電相互作用の起源を振電相互作用密度理論により解析した。

1) Y. Shigemitsu, M. Uejima, T. Sato, K. Tanaka, Y. Tominaga, *J. Phys. Chem. A*, **2012**, *116*, 9100.
2) W. Ota, M. Uejima, N. Haruta, T. Sato, *Bull. Chem. Soc. Jpn.* in press.
3) T. Kato, N. Haruta, and T. Sato, *Vibronic Coupling Density: Understanding Molecular Deformation* (Springer, 2021).