Ab Initio Study of Electron Spin-Lattice Relaxation of Triplet Oligoacenes

([1]*Graduate School of Science, Kyoto University*, [2]*CREST, JST,* [3]*FOREST, JST*) ○Katsuki Miyokawa,[1] Yuki Kurashige,[1,2,3]

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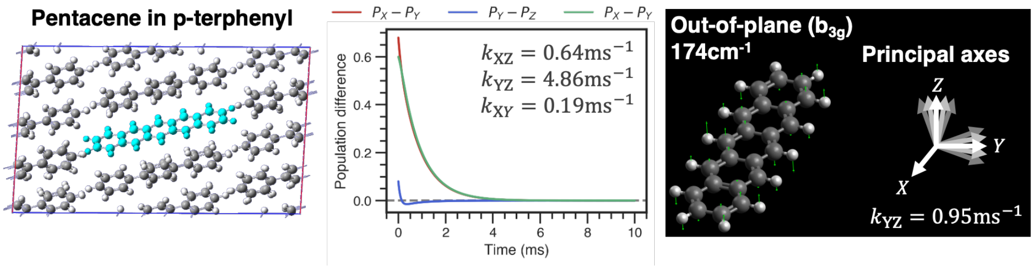
Organic chromophores are converted into triplet species through photoexcitation followed by intersystem crossing (ISC). Focusing on the spin sublevel degrees of freedom, the anisotropy of ISC rate constants for each sublevel can generate a highly spin-polarized state, which can be achieved even under room temperature and low magnetic fields. Pentacene doped in p-terphenyl host crystal is often used as a polarizing source and applied to recently emerging quantum technologies such as (1) dynamic nuclear polarization (DNP)[1], which improve the sensitivity of NMR and MRI, (2) MASER[2], and (3) high sensitivity quantum sensing[3,4]. For the molecular design of the polarizing agents, it is important to understand the mechanism of spin polarization dynamics.

Electron spin-lattice relaxation (SLR) is the process of equilibration of the population between spin sublevels and determines the lifetime of spin polarization. Despite the importance of the SLR for polarizing agents, the anisotropy of the kinetic rates of the SLR depends on the surrounding complex vibrational environment, making its mechanism elusive. Recently, spin dynamics combined with ab initio quantum chemical calculations has been applied to the molecular qubit systems and successfully revealed the microscopic mechanism of the SLR[5]. Therefore, in this study, we conducted ab initio simulations of the SLR of triplet oligoacenes using the Redfield relaxation theory where the phonon frequencies and spin-phonon couplings were determined through quantum chemical calculations. By examining the contributions of each phonon mode to the rate constants, it was suggested that the experimentally observed characteristic fast SLR between T_Y and T_Z states in pentacene originates from the out-of-plane low-frequency vibrations.



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