

Theoretical study of photoreaction mechanism based on automated exploration of minimum energy conical intersection and seam of crossing geometries

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Photo-functions, *e.g.* emission, photo-switching, and photosensitization, have been widely studied with the aim of applications. A photo-excited molecule eventually decays to the ground state by four processes, *i.e.* internal conversion via conical intersection (CI) regions, intersystem crossing *via* seam of crossing (SX) regions, fluorescence, and phosphorescence as shown in **Fig. 1**. By considering the four decay processes, it is possible to discuss any photoreactions. In the case when there is an accessible CI region (**Fig. 1a**), internal conversion can occur quickly. If there is high barrier between the Franck-Condon (FC) and CI regions (**Fig. 1b** and **1c**), intersystem crossing, fluorescence, phosphorescence processes are in competition. Therefore, to investigate the four decay processes, a systematic search for non-radiative decay paths, *i.e.* internal conversion and intersystem crossing paths, is required. However, the estimation of CI and SX geometries is not trivial.

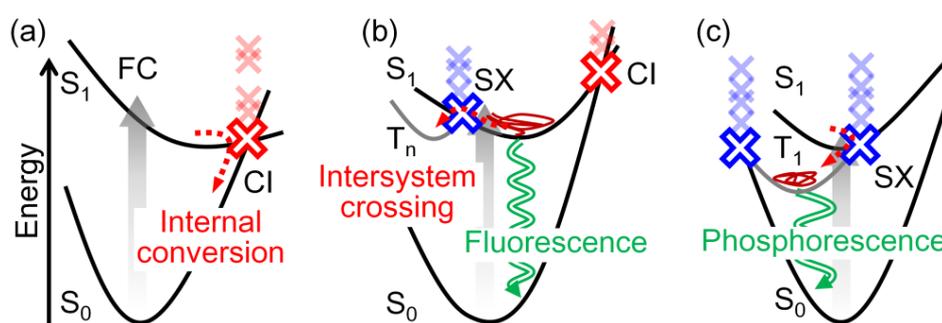


Figure 1. Schematic potential energy curves for photoreactions.

To find CI regions systematically, the seam model function (SMF) approach was proposed [1]. In the SMF, automated stable structure search methods are applied to a model function in which the local minima correspond to approximate minimum energy CI (MECI) geometries, and the obtained approximate structures are optimized. This approach has been employed extensively in studies of photodissociation mechanisms of small molecules [2]. We have extended the SMF approaches for S₁/S₀-MECIs by use of the spin-flip TDDFT (SF-TDDFT) [3, 4] in electronic structure calculations. Applicability of the SMF approach was further extended by the use of the single-component artificial force induced reaction (SC-AFIR) method [5, 6] in the automated stable structure search, and time dependent density

functional theory (TDDFT) and spin-flip TDDFT (SF-TDDFT) in electronic structure calculations [7]. Even with a small PC cluster, the method is applicable to molecules containing more than thirty atoms [7]. The automated MECI search can also be used to search for the minimum energy SXs (MESXs). Thus, all of MECIs and MESXs, i.e. any singlet-singlet, singlet-triplet, and triplet-triplet crossings can be explored automatically. Recently, an automated search for MECIs was suggested in combination with gradient projection (GP) method and SC-AFIR method [8]. The computational cost was further reduced.

As an example, the size dependence of fluorescence quantum yields in poly aromatic hydrocarbons (PAHs) was examined by applying the automated MECI search. Although there is a mild trend that the relative energy of the FC region is stabilized with the increase of the number of aromatic rings of PAH, the relative energies of the MECI points are not so much stabilized. The similar energy level for MECIs can be explained by structural deformations which are localized on a single ring. The $\Delta E_{\text{MECI-FC}}$ becomes larger with the increase of rings in PAHs, and $\Delta E_{\text{MECI-FC}}$ was well correlated with the experimental fluorescence quantum yields. Thus, the size dependence of fluorescence quantum yields is explained from the viewpoint of CI [10], which suggests that two processes, i.e., the radiative decay with emission of fluorescence (**Fig. 1b**) and the non-radiative decay through the CI (**Fig. 1a**), are in competition in these molecules.

We have applied the automated search for MECI/MESX to some photoreactions [11-13], and discussed the mechanism of them. The details of the automated MECI/MESX search and the applications will be discussed in the presentation.

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