

Development of Systematic Search Method for Non-Radiative Decay Pathways toward Designing Photofunctional Molecules

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Keywords: Conical Intersection; Seam of Crossing; Photofunctional Molecules; Automated Reaction Path Search; TDDFT

Photo-functions, *e.g.* emission, photo-switching, and photosensitization, have been widely studied with the aim of their applications, and new photofunctional molecules are being developed. For more efficient design, theoretical calculation methods are needed to provide a comprehensive understanding of molecular photoresponse based on the quantum chemical calculations.

Photoresponse of molecules can be understood by four processes, *i.e.* internal conversion, intersystem crossing, fluorescence, and phosphorescence, as shown in Figure 1. In the mechanistic analysis of photoreactions based on quantum chemical calculations, it is important to obtain the conical intersection (CI) and seam of crossing (SX) regions because non-radiative decays efficiently occur via CI and SX regions. The minimum energy CI and SX (MECI and MESX) geometries, which are the energetically most feasible points in the potential crossing regions, are normally optimized as the representative geometries of them. Especially, in studies of molecular fluorescence, it is necessary to determine the energetically most favorable internal conversion path by systematically searching for the MECI geometries and reaction paths to reach them. However, MECI geometries are normally far from the stable geometries of molecules in the ground state and the estimation of them is not trivial.

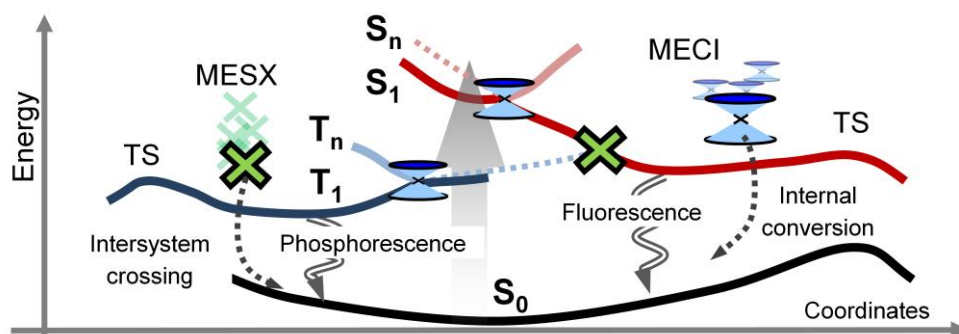


Figure 1. Schematic potential energy curves of photoreactions.

In this study, systematic and efficient search methods for MECI and MESX geometries were developed by combining the automated reaction path search methods,^{1,2} MECI/MESX optimization methods,^{1,3} and time dependent density functional theory. At the beginning of study, a search method was developed for molecules including 10 atoms⁴ and was extended

to search for molecules containing more than 30 atoms.⁵ Further, by using the density functional tight binding method, the MECI search for molecules containing more than 60 atoms became possible even with a small PC cluster.⁶ These methods enable us to systematically search for non-radiative decay pathways of molecules based on explorations of MECI and MESX geometries.

The present methods were applied to various type of photofunctional molecules, and the importance of a non-radiative decay path search was demonstrated. As an example, internal conversion paths of poly aromatic hydrocarbons (PAH) were examined based on the S_1/S_0 -MECI search, and the difference in the experimental fluorescence quantum yields of PAH was explained from the viewpoint of barrier height along internal conversion paths.⁷ It was also shown that the discussion based on such barrier height can be applied to relatively large molecules through a study of macrocyclic aromatic molecules.⁸ Furthermore, the methods were applied to discuss the difference of the intersystem crossing quantum yields of heteroaromatic compounds.

Explorations of non-radiative decay pathways were also effective in the mechanistic analysis of ultrafast decay processes of molecules.⁹ Ultrafast decay mechanisms of molecules were discussed based on the comparison between the results of obtained non-radiative decay pathways and time-resolved spectroscopic experiments. The present methods were applicable to photoreactions of metal complexes where both singlet and triplet states are related.¹⁰ Recently, rate constants of the reverse intersystem crossing process were predicted based on MESX geometry optimization,¹¹ and it was shown that the predicted rate constant can be used for designing molecules. The search methods for the non-radiative decay pathways and their applications will be discussed in the presentation.

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