Automated search for nonradiative pathways in molecules and organometallic complexes

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Nonradiative decay occurs efficiently on the intersection hypersurface between two adiabatic potential energy surfaces (PES) of different electronic states, where those between states of the same spin and space symmetry are called conical intersection (CI), otherwise they are called seam of crossing (SX). Minimum energy CI (MECI) and minimum energy SX (MESX) structures have been calculated as energetically most preferable points within the CI or SX hypersurface. By identifying the lowest MECI and MESX structures among those accessible from the Franck-Condon (FC) structure, whether the system has any fast nonradiative decay process or not can be predicted. When all MECI and MESX structures are high in energy, the system stays on the electronic excited state for a long time and shows strong emission. It is also possible to qualitatively discuss the mechanism of nonadiabatic transition. Therefore, a theoretical approach locating all accessible MECIs and MESXs has been desired.

We have developed an automated MECI / MESX search method, based on the artificial force induced reaction (AFIR) method.[1] The AFIR method has been developed for the automated search of local minimum and transition state structures on the ground electronic state.[2] By combining the AFIR method with MECI / MESX geometry optimization techniques, the automated search for these structures has become possible. Fig. 1 shows a list of S_0/S_1-MECI structures of coumarin between the lowest and first excited singlet electronic states. In photoreaction of coumarin in gas-phase, the nonadiabatic path via a ring-opened intermediate has been known to be dominant, and such MECIs were found to be the two most stable MECIs in the automated search.[1] In addition, many low-lying MECIs were found systematically, as seen in Fig. 1.

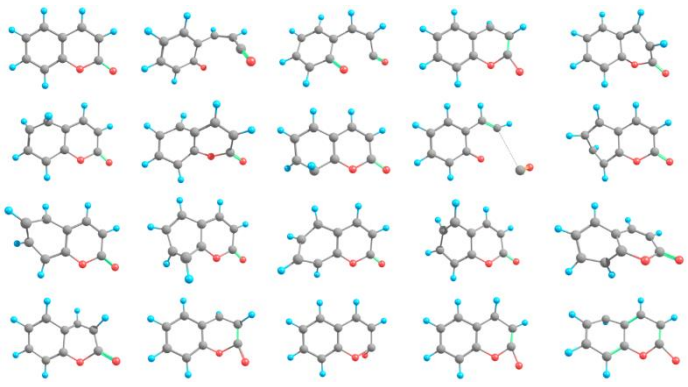

Figure 1. The FC structure of coumarin (top left) and S_0/S_1-MECI structures around the FC structure obtained by the automated search using the AFIR method.[1a]

The present approach has been applied to various molecules such as small polyaromatic hydrocarbon (PAH) molecules,[3] α-pyrone,[4] Re(I)-complexes,[5,6] furan and dibenzofuran,[7] and methylcinnamate.[8] Based on obtained MECIs and MESXs, photoreactions these molecules have been discussed in detail. In my talk, these application results will be discussed in detail, after brief introduction of the automated MECI /MESX search method.

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