

## 2P086 **Theoretical study of the spin-forbidden reaction of the transition metal complex**

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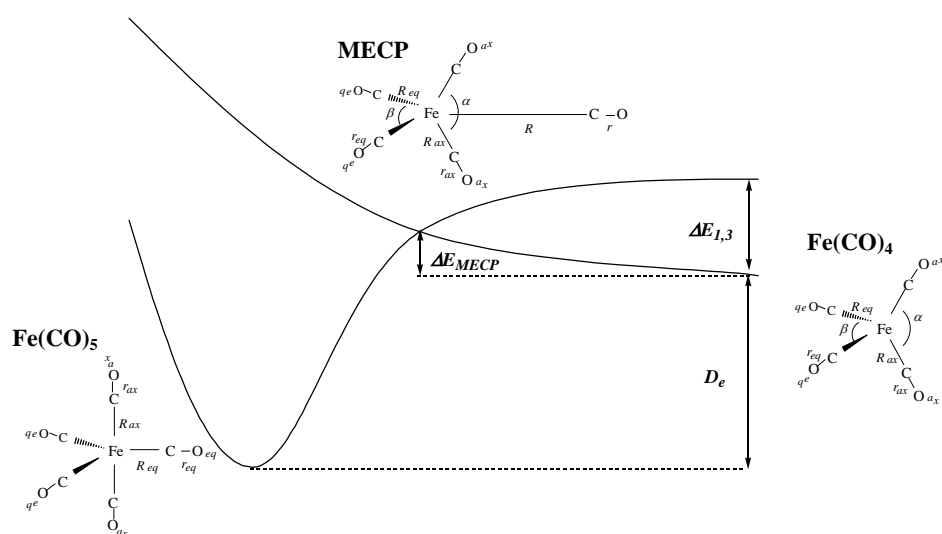
The composition reaction of the iron pentacarbonyl from iron tetracarbonyl and carbon monoxide, on which we have focused in this study, is a spin-forbidden reaction. The total spin multiplicity of the system changes as the reaction goes from the reactant, triplet, to the product, singlet. This kind of reaction is theoretically forbidden, however, frequently occurs in nature. This can be attributed to the spin-orbit coupling which enables the mixing of states of different spin multiplicities, which is, however, not allowed in the nonrelativistic or scalar-relativistic framework. In the limit of no spin-orbit coupling, the system is represented to be diabatic, in which two potentials of different spin cross each other without interacting, and the transition between two potentials is strictly forbidden. In another limit of the strong spin-orbit coupling, reaction proceeds on the adiabatic potential surface which smoothly connects the reactant and the product of different spin multiplicities. Iron carbonyl complex form a system of intermediate spin-orbit coupling in which the spin-orbit interaction is modest, which possesses nonadiabatic potentials. To locate the transition state of the nonadiabatic reaction, it is a reasonable and convenient approximation to treat the system as a diabatic system when the avoided crossing is small enough to be inconsiderable since the spin-orbit interaction is weak enough that it hardly affects the entire potential surfaces, which is actually the case we have had for the iron system, and since the complete treatment of the spin-orbit coupling in the current theoretical methodology to locate the adiabatic transition state is not trivial. Then, the problem of locating the transition state of the nonadiabatic reaction is reduced to the problem of simply locating the crossing point of two diabatic potential surfaces, which is sometimes referred as the minimum energy crossing point (MECP).

Through the long way of investigating the methodology for optimizing the MECP on the nonadiabatic potential surfaces, it has been known that the usage of the gradient should be the most effective way in practice. The ordinary transition state search and the equilibrium geometry optimization schemes, which have been accepted as powerful methods, have already been well developed taking advantage of the gradient method. Our experience of the effort for locating the MECP by manually constructing potential surfaces from the set of a large number of single point energy calculations for both states, which actually has been the major methodology in the ancient world, has led us to the same conclusion. However, unlike the ordinary transition state search and the equilibrium geometry optimization, the application of the gradient method for the automatic optimization of the MECP is not very simple since there is no trivial stopping

condition, such as the gradient should be exactly zero, after the optimization's arriving at the proper point on the potential surfaces. However, realizing and making use of the fact that the MECP is merely the minimum energy point within the sub space, the seam where two potential surfaces cross, and thus, the total energies of two states are the same within the seam makes it possible to locate the MECP in the usual way by simply adding one constraint with respect to the equality of the total energy of two states. The constrained optimization can be done by the lagrangian method. In our study, we have employed the lagrangian consists of the total energy of one state, Frank-Condon state, and the total energy equality condition and minimized it with respect to the coordinates and the lagrangian multiplier.

It is well known that the dynamical electron correlation as well as the degeneracy effect is important for the accurate calculation for the system containing transition metal elements. The CASPT2 method has been shown to be capable to provide a reliable result for the transition metal element systems. We have employed the scalar-relativistic CASPT2 method to describe the diabatic potentials for the iron pentacarbonyl system. As stated previously, the gradient plays an important roll to efficiently optimize the MECP, however, the analytical gradient for the CASPT2 is not currently available as well as the numerical gradient is not practical since the single point energy calculation is already heavy itself. For the purpose of overcoming this deficiency, we have developed the method to use the approximate gradient calculated from the approximate surfaces constructed by fitting the potentials to the second-order polynomials.

We have applied our method to the iron pentacarbonyl system and investigated the geometries and energetic properties shown in **Figure 1**.



**Figure 1.** Schematic representation of the nonadiabatic reaction system.