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# Theoretical Investigation of photoisomerization mechanisms of N-salicilydenemethylfurylamine (SMFA)

Ai-Hua Gao, and Meishan Wang*

*School of Physics and Optoelectronic Engineering, Ludong University, Yantai 264025, China*

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**Abstract.** TExcited state reaction coordinates and the consequent energy profiles of a new Schiff base, N-salicilydenemethylfurylamine (SMFA), have been investigated with the MP2 and CASSCF method. The potential energy profiles of the ground and the lowest excited singlet state are calculated. The excited state potential energy profile shows a small barrier in the LIIC pathway of dissociation along the O-H stretching coordinate. This work suggests that there are two pathways in the photochemical reaction of SMFA. In one pathway, the photochemical product is the enol-type minimum. In the other pathway, the ESIPT reaction is observed and a excited state stationary structure is reached. The trans-keto and cis-keto type structures will be obtained from photoexcitation of the enol isomer. Two conical intersections between the ground and excited states act as the gates for nonadiabatic decay to the ground state.

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**Key words**: excited state reaction, ESIPT, photochromoic effect, SMFA, photoisomerization mechanism.

## 1 Introduction

Photochromism in organic molecules [1-2] is a kind of very important photochemical phenomenon and well-known to be among the ultrafast chemical reactions occurring in nature. Upon excitation, the stable form of a photochromic compound in the ground state tends to be a metastable form (excited-state minimum or conical intersection between two states). The molecule eventually reverts to original structure or converts to the other stable form in the ground state. The reversible cyclic nature of this process is the key feature of their importance in technical applications in the fields of photochemical area.

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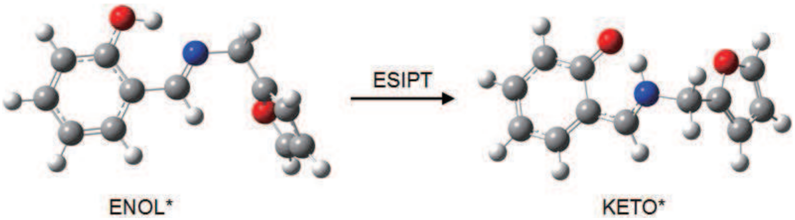
*Corresponding author. *Email address:* `mswang1971@163.com` (M. S. Wang)

Photochromism includes ultrafast processes such as cis-trans or trans-cis photoisomerization, [3-4] photochemical ring-closure-ring-opening reactions, [5-6] or excited-state intramolecular proton transfer (ESIPT). [7]

The photochromic processes of aromatic Schiff bases have been widely investigated since they play particularly important roles in the photochemistry area. These compounds can be used as logic devices, optical data processing, molecular motors, etc. [8-13] In aromatic Schiff bases, the mechanism and dynamics of ESIPT (from the original excited enol form to the keto form) and the creation of photochromic tautomer is concerned about in the investigations. These ultrafast dynamic reactions may be accompanied with other photochemical processes such as cis-trans or trans-cis photoisomerizations, internal conversion through conical intersections (CIs) or avoided crossing between two states.



Scheme 1: Molecular structures of enol (ENOL$^*$) and keto (KETO$^*$) tautomers of SMFA at the $S_1$ state.

Investigations should be done to understand the excited states of Schiff bases for the importance of photophysics of these compounds. However, very few studies has been done on the photophysics of Schiff bases yet. Jankowska and coworkers investigated the proton-transfer reaction in a model aromatic Schiff base, salicylidene methylamine (SMA), in the $S_0$ and $S_1$ states. There are two $S_1/S_0$ CIs between the $S_0$ and $S_1$ states which act as nonadiabatic gates for a radiationless decay to the $S_0$ state. Their calculations indicated that aromatic Schiff bases are potential candidates for optically driven molecular switches. [14] A theoretical study was reported on the photochemistry of salicylideneaniline in the gas phase using static electronic structure calculations and surface hopping dynamics simulations by Spörkel and coworkers. [15] Upon photoexcitation of the most stable cis-enol tautomer into the $S_1$ state, an ultrafast ESIPT was found in agreement with the work done by Ortiz-Sánchez. [16] The internal conversion is initiated by an out-of-plane motion around the C-C single bond. The molecule moves toward a CI providing an efficient deactivation channel to the $S_0$ state. Equal amounts of the $S_0$ cis-enol and trans-keto photoproducts were obtained by the dynamic simulations. Spörkel *et al*. demonstrated that the $S_1$ cis-keto form and the stable $S_0$ trans-keto one is responsible for fluorescence and photochromism, respectively. Recently, Moghadam *et al*. investigated the photophysics of a new Schiff base, N-salicilydenemethylfurylamine (SMFA), with the CC2 method. [17] The excited state potential energy profile shows a barrier-less dissociation pattern along the O-H stretching coordinate which verifies the proton transfer reaction at the first singlet excited ($S_1$) state (see scheme 1). The calculations indicate two CIs between the $S_1$ state and ground ($S_0$) state play important parts in nonadiabatic decay