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One dimensional Kramers-Grote-Hynes-based reaction rate analysis on thermally bleaching process of spirooxazines

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I. Abstract

Photochromism of spirooxazines is initiated by fast photo-induced ring-opening reaction on the excited state potential energy surface (PES) accompanied with colouration, followed by slow thermally backward ring-closing reaction on adiabatic ground state PES. We herein report the analysis on the reaction rate using a variation of generalized-Langevin-equation models, i.e., Kramers-Grote-Hynes (k_KGH) and Pollak-Grabert-Hanggi (k_PGH) within one dimensional freedom. The aim of this presentation is to adequately describe the abnormal turnover incompatible with the Kramers turnover within one dimensional model.

I. Introduction

The thermal bleaching mechanism of spirooxazines has been extensively examined from both theoretical and experimental viewpoints. In condensed phase such as in the organic solvent, its reaction rate deviates from that of transition state theory (k_TST) under a very high pressure with extremely strong solvent viscosity. Dating back to Kramers theory, the deviation has been analyzed on some theoretical models such as a variant of Fokker-Plank equation, where fast (solute vibration) and slow (solvent fluctuation) mode are independently treated to adequately describe the abnormal behavior of so-called Kramers turnover. Within this model, however, the diffusion equation is described by macroscopic parameters (simple model potential of mean force) and lacks the detailed information on molecular systems. The one dimensional model reported here include only one freedom along the reaction path coordinate and no consideration to decouple several freedom such as slow fluctuation or other non-reactive freedom. The reverse interconversion of spirooxazines is considered to hold strong solute-solvent coupling and expected to be well-described within one-dimensional model.

II. Results and discussion

We solve the so-called Kramers and Grote-Hynes equations to evaluate the reaction rate. In PGH theory, we furthermore solve the depopulation factor to evaluate the reaction rate. As a solvent friction kernel, we use the Laplace transformed expression of Gaussian-type friction.
The magnitude of friction is regulated by varying the two parameters; the frequency ratio of solute-solvent at the saddle-point and a friction strength parameter ($\alpha$). PGH is useful in uniformly describing the dependency of reaction rate on solvent friction from the range of low-pressure (increasing rate) to that of high pressure limit (decreasing rate). As a figure shows, $k_{\text{PGH}}$ has bell-shaped structure as function of $\alpha$, which indicates the energy dissipation is important during the motion along the reaction path.

\[ k_{\text{PGH}} = \frac{\lambda_{\text{PGH}}}{\omega} k_{1D-TST} \]

\[ k_{\text{PGH}} = \frac{\lambda_{\text{PGH}}}{\omega} k_{1D-TST} Y(\alpha, t_d, \lambda_{\text{PGH}}) = k_{\text{PGH}} Y(\alpha, t_d, \lambda_{\text{PGH}}) \]

References