Theoretical Investigation of the Chemiexcitation Step of Chemi/Bioluminescent Reactions

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Chemi-/bioluminescence are processes that consist of the conversion of thermal energy into light-emission, as the result of a (bio)chemical reaction.[1] Both processes have the advantage of not needing photoexcitation, which diminishes the possibility for autofluorescence arising from the background signal. The absence of photoexcitation also eliminates problems associated with light-penetration into biologic tissue. Thus, these systems have been used in the real-time imaging of target molecules and processes, both *in vivo* and *in vitro*.[1]

While the mechanism that allows for the generation of singlet excited states without photoexcitation (also known as chemiexcitation) is not fully understood, it is known that chemiexcitation occurs during the thermolysis of cyclic peroxide intermediates.[2,3] Herein, we performed a theoretical investigation of the chemiexcitation step of prototypical cyclic peroxides, by employing reliable and up-to-date methodologies based on time-dependent (TD)-density functional theory (DFT) and multireference calculations.[2,3]

Our results showed that efficient chemiexcitation results from the decomposing molecules having access to a large and flat biradical region of the potential energy surface (PES) where the singlet ground and excited states are degenerated. Use of the activation strain model and Born-Oppenheimer molecular dynamics indicated that access to this region of degeneracy is provided by increasing interaction between the thermolysis' molecular fragments, which extends the biradical region by delaying the rupture of the peroxide ring.[2,3]

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References

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