
Unraveling the chemiluminescence yield of 1,2-dioxetanes

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Abstract

Chemiluminescence is the emission of light as a result of a non-adiabatic chemical reaction. One of the simplest molecules with chemiluminescent properties is 1,2-dioxetane. While the yield of the chemiluminescent process is observed to be low in 1,2-dioxetane (approximately 0.3%), it increases to 35% by substituting the hydrogen atoms by methyl groups. More than 30 years after the measurements, the reason for the impressive increase in chemiluminescence yield with the degree of methylation remains an outstanding question. The aim of the present work is to address it, using simple and accessible concepts. Both ground-state and non-adiabatic dynamics (including singlet excited states) of the decomposition reaction of various methyl-substituted dioxetanes have been simulated, starting from the first O–O bond-breaking transition structure. The simulations show that methyl-substitution leads to a significant increase in the dissociation half-life: 58 fs for the un-methylated dioxetane, while 117 fs for the tetra-methylated compound. This is because the rotation around the central O–C–C–O dihedral angle is slowed down by the "heavy" methyl groups. As a consequence, the molecular system stays longer in the so-called "entropic trap" region where a manifold of states are degenerate, and more population is transferred into the excited state of the product before dark decomposition occurs. A simple kinetic model is proposed to explain the resulting higher chemiluminescence yield.

Keywords: dioxetane, non adiabatic dynamics, surface hopping, multi reference electronic structure methods

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