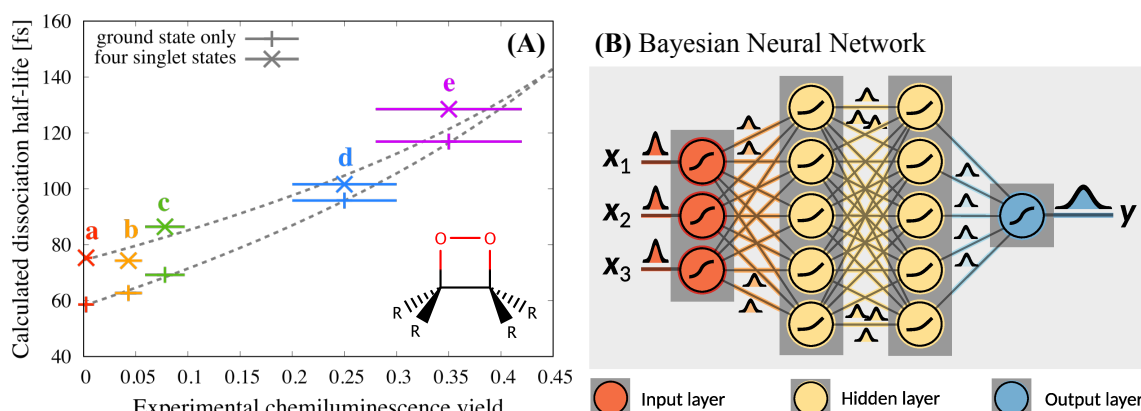


# Insights into chemiluminescence from molecular dynamics simulations and machine learning analysis

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Chemiluminescence is the emission of light as a result of a non-adiabatic chemical reaction [1,2]. It can be seen as a “reversed” photochemical process. 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 has remained an outstanding question. In the first part of the presentation, we will address it using ground-state and non-adiabatic dynamics of the decomposition reaction [3,4]. The simulations show that methyl-substitution leads to a significant increase in the dissociation half-time. 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 (figure 1A). While simulations are often key to the understanding of chemical reactions, a current challenge is the in-depth analysis of the large amount of data produced, in order to provide valuable insight. In the second part of the presentation, we will present machine learning models trained to predict directly a specific outcome quantity of ab initio molecular dynamics simulations of chemiluminescent reactions (figure 1B). Our results show that in order to make accurate predictions, the models evidence empirical rules that are, today, parts of the common chemical knowledge [5]. This paves the way for conceptual breakthroughs in chemistry where machine analysis would provide a source of inspiration to humans.



**Figure 1:** (A) Molecular dynamics simulations of the decomposition of 1,2 dioxetane. (B) Bayesian neural network trained to reproduce the molecular dynamics results.

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