MOLECULAR DYNAMICS OF PHOTOCHEMICAL PROCESSES

Morgane VACHER

Department of Chemistry – Ångtröm, Uppsala University, Sweden
morgane.vacher@kemi.uu.se

A photochemical process is a chemical reaction that is caused by the absorption of light and involves several electronic states. In this presentation, we will focus on two types of photochemical processes.

In the first part, we will discuss coherent electron dynamics following photoionization of molecules (Figure 1a). The hope to observe electronic motion on its own time scale arose a few years ago in the field of attoscience.[1] A fundamental question remains the factors influencing electronic decoherence and the role played by nuclear motion in this process. Here, we have simulated the dynamics upon ionization of polyatomic molecules, with a quantum mechanical treatment of both electron and nuclear dynamics using the direct dynamics variational multiconfigurational Gaussian method.[2] Our simulations have shown that the decoherence of electron dynamics happens on the time scale of a few femtoseconds, with the interplay of different mechanisms.[3]

In the second part of the presentation, we will discuss a "reversed photochemical process", called chemiluminescence, where the emission of light results from a non-adiabatic chemical reaction.[4,5] The present work is concerned with understanding the yield of chemiluminescence, in particular how it dramatically increases upon methylation of 1,2-dioxetane. Our ground state and non-adiabatic surface hopping dynamics simulations have shown that dark decomposition takes more time upon methylation of 1,2-dioxetane, due to a simple mass effect.[6] The longer the system stays in the entropic trap, the more population is transferred from the singlet ground state to the triplet states and the higher the chemiluminescence yield is (Figure 1b).

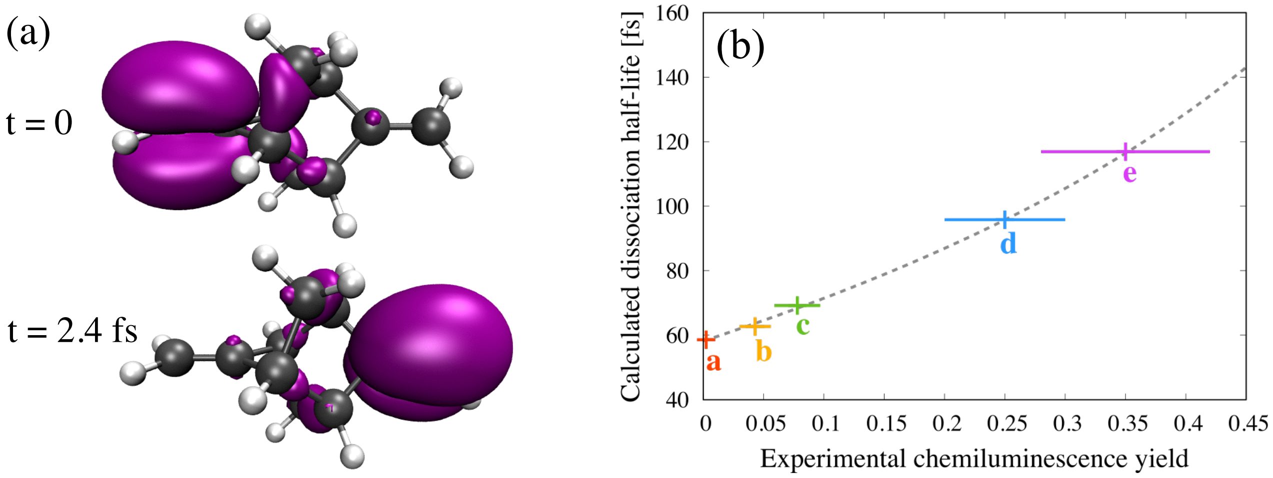

Figure 1: (a) Coherent electron dynamics upon valence ionization of a modified bis-methylene adamantane. (b) Increase of the experimental chemiluminescence yield of dioxetane upon methyl-substitution due to a slower decomposition: compounds a, b, c, d and e have 0, 1, 2, 3 and 4 methyl groups respectively.

1. F. Calegari et al, *Science*, 346, 336, **2014**.
2. M. Vacher, M. J. Bearpark and M. A. Robb, *Theo. Chem. Acc.*, 135, 187, **2016**.
3. M. Vacher, M. J. Bearpark, M. A. Robb and J. P. Malhado, *Phys. Rev. Lett.*, 118, 083001, **2017**.
4. I. Navizet, Y.-J. Liu, N. Ferré, D. Roca-Sanjuán and R. Lindh, *Chem. Phys. Chem.*, 12, 3064-3076, **2011**.
5. M. Vacher, A. Brakestad, H. O. Karlsson, I. Fdez. Galván and R. Lindh, *J. Chem. Theory Comput.*, 13, 2448-2457, **2017**.
6. M. Vacher, P. Farahani, A. Valentini, L. M. Frutos, H. O. Karlsson, I. Fdez. Galván and R. Lindh, *J. Phys. Chem. Lett.* 8, 3790-3794, **2017**.