

Investigating *in silico* the sunlight-triggered excited-state dynamics of transient atmospheric molecules

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Volatile organic compounds (VOC) are ubiquitous atmospheric molecules which generate a complex network of chemical reactions in the troposphere, often triggered by absorption of sunlight. Since the short lifetime of some transient VOCs poses significant challenges for accurate experimental and spectroscopic measurements, there is an urgent need for predictive computational approaches to study VOCs, in particular when it comes to their photochemistry and photophysics.

First, we show how recent advances in computational photochemistry allow us to calculate *in silico* photolysis rate constants.[1] Such rate constants are utilized in general atmospheric models used to predict the accurate composition of atmosphere but are often not experimentally available for transient VOCs. Photolysis rate constants depend on three key pieces of information: the flux of the radiation source, the photoabsorption cross-section of the molecule and the wavelength-dependent photolysis quantum yield. We show how one can evaluate the sought-for ingredients – and consequently the corresponding photolysis rate constants – by combining state-of-the-art electronic structure methods (XMS-CASPT2) and nonadiabatic molecular dynamics methods (surface hopping). We benchmark our protocol with the photolysis of *tert*-butyl hydroperoxide, a compound for which reliable experimental data are available.[2]

In addition, we investigate the photodynamics of molecules bearing a carbonyl group, which concerns a large class of VOCs, as well as other important molecules such as nucleobases. In this context, we demonstrate a systematic flaw of the popular electronic structure method ADC(2) for such carbonyl-containing compounds, leading to artificial deactivation pathways.[3]

References:

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