

# Non-adiabatic molecular dynamics simulations of photochemical isoprene oxidation intermediates

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Isoprene is amongst the most abundant volatile organic hydrocarbon compounds in the atmosphere, with annual biogenic emissions that are comparable to methane. Nevertheless, our understanding of its atmospheric oxidation sequence is not yet complete. [1] Assorted pieces of indirect evidence suggest that intermediates produced during isoprene oxidation produce OH via an as yet undetermined photochemical mechanism. [2] In this talk, I will describe new work designed to investigate the photochemical molecular dynamics (MD) of both C5-hydroperoxy-aldehyde (C5-HPALD) and C6-HPALD (a relative of C5-HPALD which has been synthesized and measured in the laboratory). [3] C5-HPALDs are isoprene oxidation intermediates which have been hypothesized to photolytically produce OH. Using a range of excited state quantum chemistry methods, we have characterized the excited electronic states of both C5 and C6 HPALD, and calculated their corresponding excited state absorption cross sections. Our results quantitatively reproduce experimentally measured photolysis rate coefficients for C6-HPALD. [3] For both C5 and C6 HPALDs, a weak  $S_1 \ n \rightarrow \pi^*$  absorption feature is largely responsible for the photolysis rate coefficient observed under ambient atmospheric conditions. Exploiting a fast GPU-accelerated TDDFT framework, we ran semi-classical non-adiabatic MD simulations initialized in the C5 HPALD  $S_1$  state. The results indicate two competing mechanisms which are responsible for picosecond-timescale population transfer out of the  $S_1$  state: (1) internal conversion via avoided crossing to an  $S_2$  state with  $\sigma^*$  character, and (2) intersystem crossing to a low-lying triplet state with  $\sigma^*$  character. Both of these states appear to lead to fast bond dissociation and OH production. In order to understand how the *in vacuo* MD kinetics map onto atmospheric temperatures and pressures, we have used the MESMER non-equilibrium statistical mechanics package to construct an energy-grained master equation of C5-HPALD using a non-adiabatic variant of microcanonical transition state theory (TST). The non-adiabatic master equation framework allows us to investigate the photochemical kinetics of C5-HPALD photochemistry under typical atmospheric temperatures and pressures, and provides direct evidence for OH production in near unity quantum yield.

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## References

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