

# Role of nuclear quantization for *ab initio* modeling of methyl iodide photodissociation

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Light can activate, direct, and speed up chemical reactions otherwise inaccessible by conventional reaction conditions like heat. Photodissociation is the decomposition of a molecule as the result of photoexcitation. Multiple basic mechanisms and processes contributing to photolysis can be explored by quantum mechanical analysis of methyl iodide. This 5-atom molecule allows for a detailed analysis of the quantum dynamics of its nuclei in the excited electronic state. Here we use methyl iodide to computationally compare photodissociation trends calculated by the dynamics of coupled electronic and nuclear degrees of freedom by two methods and two regimes via wavepacket methods for a single molecule and by time-dependent excited state molecular dynamics (TDESMD) methods<sup>1</sup> for an ensemble of eight methyl iodide molecules. The results of our computations indicate that for time scales shorter than 50 fs the two approaches for two modes provide similar conclusions for the photodissociation event. However, the results of the two methods diverge after 50 fs likely because the TDESMD method likely indicates an event of a molecular collision. Therefore, we conclude that either approach is suitable for modeling the photodissociation of methyl iodide at a short time interval after the photoexciting pulse. At the relatively long-time delay, each of the methods provides additional aspects of dynamics. Wavepacket method is able to show wavepacket cloning and superpositional Schrödinger cat states, confirmed experimentally. The TDESMD method allows the description of higher density models, ensembles of reactant molecules and more variety of reactions involving collisions. Both methods have to be used simultaneously as they provide complementary picture of the photo reaction mechanisms

<sup>1</sup> Han, Y.; Meng, Q.; Rasulev, B.; May, P. S.; Berry, M. T.; Kilin, D. S., Photoinduced Charge Transfer Versus Fragmentation Pathways in Lanthanum Cyclopentadienyl Complexes. *Journal of Chemical Theory and Computation* **2017**, *13*, 4281-4296