

Photofragmentation of Tetranitromethane: Spin-Unrestricted Time-Dependent Excited-State Molecular Dynamics

Yulun Han^{1,2}, Bakhtiyor Rasulev³, Dmitri S. Kilin^{1,2}

¹Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND 58108

²Department of Chemistry, University of South Dakota, Vermillion, SD 57069

³Center for Computationally Assisted Science and Technology, North Dakota State University, Fargo, ND 58102

The exploration of photoinduced reactions is a great challenge and a practical demand. Tetranitromethane (TNM) has a wide range of applications. For example, it can be used as a nitrating reagent for a preferential modification of proteins and as an analytical reagent for detection of double bonds in organic compounds. In this study, TNM is used as a test model. The photofragmentation dynamics of TNM is explored by a novel *spin-unrestricted time-dependent excited-state molecular dynamics* (u-TDESMD) algorithm based on Rabi oscillations and trajectory surface hopping, with a mid-intensity field approximation.^{1,2} The leading order process is represented by the molecule under cyclic excitations and de-excitations. During excitation cycles, the kinetic energy is accumulated to overcome the dissociation barriers in reactant and a sequence of intermediates. The computed results show drastically different reaction pathways for open-shell and closed-shell electronic configurations. Specifically, the simulation using neutral closed-shell TNM as a starting point illustrates mostly single NO₂ ejection pathway. The simulation using cationic open-shell TNM⁺ as a starting point shows an extensive cracking pathway in addition to sequential NO₂ ejection. The simulated mass spectra at the *ab initio* level, based on the bond length of possible fragments are extracted from simulation trajectories. The computed *ab initio* mass spectra with different starting points might shed light about whether the so-called “ladder switching” or “ladder climbing” process dominates when the molecule interacts with a laser field. The recent-developed methodology has the potential to model and monitor photoreactions with open-shell intermediates and radicals.

References

1. Han, Y.; Kilin, D. S.; May, P. S.; Berry, M. T.; Meng, Q., Photofragmentation Pathways for Gas-Phase Lanthanide Tris(isopropylcyclopentadienyl) Complexes. *Organometallics*, 2016, 35, 3461.
2. Han, Y.; Meng, Q.; Rasulev, B.; May, P. S.; Berry, M. T.; Kilin, D. S., Photofragmentation of the Gas-Phase Lanthanum Isopropylcyclopentadienyl Complex: Computational Modeling Vs Experiment. *J. Phys. Chem. A* 2015, 119, 10838.