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

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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 \textit{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.\textsuperscript{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 NO\textsubscript{2} ejection pathway. The simulation using cationic open-shell TNM\textsuperscript{+} as a starting point shows an extensive cracking pathway in addition to sequential NO\textsubscript{2} ejection. The simulated mass spectra at the \textit{ab initio} level, based on the bond length of possible fragments are extracted from simulation trajectories. The computed \textit{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