DOCTORAL THESIS

Light-driven molecular rotary motors

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Date of Award:
2017

ABSTRACT

In the past two decades, a number of artificial molecular motors have been constructed using organic molecules as components which can perform unidirectional motion. Among the best-known examples are the light-activated molecular rotary motors synthesized and analyzed in B. L. Feringa's lab. Yet there is limited understanding of the photoisomerization and thermal isomerization processes that control the speed and energy conversion efficiency of these molecular devices. The present thesis work aims at: 1) developing a computational methodology to provide the atomic and electronic details that allow for quantitative descriptions of light-activated molecular motion, 2) improving the understanding of the physical principles governing photo- and thermal-isomerization processes in specific molecular systems, and 3) proposing a new strategy of molecule design to assist experimental investigations.

A key component in our methodology is the calculation of the potential energy surface (PES) spanned by collective atomic coordinates using *ab initio* quantum mechanical methods. This is done both for the electronic ground state, which is relatively straightforward, and for the photo-excited state, which is more involved. Once the PES is known, classical statistical mechanical methods can be used to analyze the dynamics of the slow variables from which information about the rotational motion can be extracted. Calculation of the PES is computationally expensive if one were to sample the very high dimensional space of the atomic coordinates. A new method, based on the torque experienced by individual atoms, is developed to capture key aspects of the intramolecular relaxation in terms of angular variables associated with the rotational degrees of freedom. The effectiveness of the approach is tested on specific light-driven molecular rotary motors that were successfully synthesized and analyzed in previous experiments.

Finally, based on the experience accumulated in this study, a new molecular rotary motor driven by visible light is proposed to reach MHz

rotational frequency.

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