Probing Light-Induced Isomerization Dynamics of Azobenzene Confined within Metal-Organic Frameworks: A Time-Dependent Density Functional Theory Investigation

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ABSTRACT SUBMISSION

Metal-organic frameworks (MOFs) have garnered significant attention for their tunable structures and potential applications in chemistry, physics, and materials science. Among these, metal-organic responsive frameworks (MORFs)[1] offer new opportunities by leveraging light-actuated behavior for applications in sensing, catalysis, drug delivery, and carbon capture. This research focuses on azobenzene, a prototypical photoisomerizing molecule, and its behavior under confinement within MOFs. Using time-dependent density functional theory (TD-DFT), we investigate the trans-to-cis and cis-to-trans photoisomerization pathways and how they are influenced by external factors such as excitation wavelength, solvent effects, and steric constraints.

We have completed ground-state optimizations of azobenzene in vacuum, benzene, and water, as well as excited-state calculations for the first two singlet states in vacuum. All calculations have been performed using the Gaussian16 software [2]. Our results are consistent with prior studies, both experimental and computational, particularly those by Crecca and Roitberg [3], in confirming that the trans isomer is more stable than cis by ~0.6 eV, and that the cis to trans isomerization barrier in the ground state is 1.08 eV.e explore the role of conical intersections, electronic relaxation pathways, and quantum yield variations to better understand the dominant isomerization mechanisms under different conditions. By elucidating the influence of confinement on electronic structure and isomerization efficiency, this study aims to help establish design principles for optimizing MORFs for practical applications. We anticipate to further present calculations of azobenzene within a 3D-MOF to further explore the impacts of constraint in the isomerization process.

ACKNOWLEDGMENT

We would like to express our sincere thanks to the University of Wyoming's Research Scholar Program for providing funding for this research. The scientific computing resources of this work were supported by the Advanced Research Computing Center (ARCC) at the University of Wyoming and the National Center for Atmospheric Research Wyoming Supercomputer (NWSC), allocation WYOM0181.

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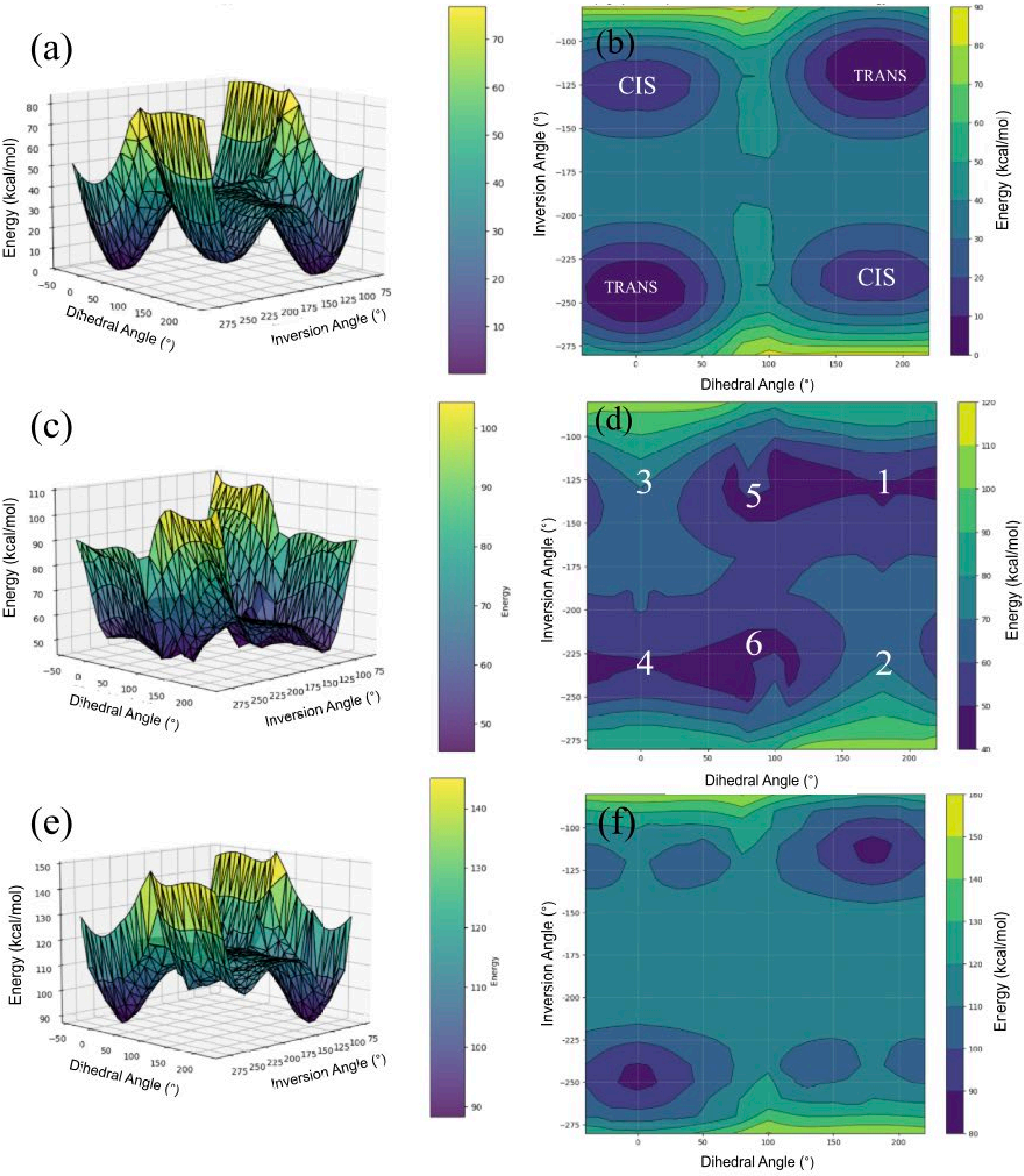

Figure 1 (a) Potential energy surface and (b) contour map of the ground state of Azo. The cis and trans minima are also labeled. (c) Potential energy surface and (d) contour map of the first excited state of Azo. Points 1 and 4 represent where the molecule is on the S1 surface after excitation from the ground-state trans minima, whereas excitation from the ground-state cis minima will place in the molecule at points 2 and 3. Points 5 and 6 represent the S1 minima as well as mark the location of the S1/S0 conical intersection. (e) Potential energy surface and (f) contour map of the second excited state of Azo. All angles are in degrees and energy is in kcal mol-1, relative to the energy of the ground state trans isomer.