

UNRAVELING THE MECHANISM OF THE ELECTRONIC QUENCHING OF NO ($A^2\Sigma^+$) WITH C₂H₂

KEN JONES, ANDREW S. PETIT, *Department of Chemistry, California State University, Fullerton, Fullerton, CA, USA.*

NO is an important reactive intermediate in combustion and atmospheric chemistry. The experimental detection of NO commonly utilizes laser-induced fluorescence (LIF) on the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition band. However, the electronic quenching of NO ($A^2\Sigma^+$) with other molecular species provides alternative photochemical pathways that compete with fluorescence. Prior experimental studies have demonstrated that collisions with C₂H₂ are effective at driving the non-radiative relaxation of NO ($A^2\Sigma^+$). Moreover, H-atom production has been observed in this electronic quenching. However, no detailed experimental or theoretical studies have been performed on this system, and the specific photochemical pathways of NO ($A^2\Sigma^+$)+C₂H₂ remain unexplored.

Here, we describe the development of high-quality potential energy surfaces (PESs) that provide new physical insights into the long-range interactions and conical intersections that facilitate the electronic quenching of NO ($A^2\Sigma^+$) by C₂H₂. The PESs are calculated at the EOM-EA-CCSD/d-aug-cc-pVTZ//EOM-EA-CCSD/aug-cc-pVDZ level of theory, an approach that ensures a balanced treatment of the valence and Rydberg electronic states as well as an accurate description of the open-shell character of NO. We demonstrate that intermolecular interactions between NO ($A^2\Sigma^+$) and C₂H₂ cause C₂H₂ to isomerize into its *trans*-bent confirmation. We further identify a downhill pathway for internal conversion. Finally, we are beginning to explore the role that low-lying electronic excited states of C₂H₂ play in the electronic quenching of NO ($A^2\Sigma^+$) by C₂H₂. Our work informs future velocity-map imaging experiments and non-adiabatic dynamics simulations on this system.