UNRAVELING THE MECHANISM OF THE ELECTRONIC QUenchING OF NO \( (A^2\Sigma^+) \) WITH C\(_2\)H\(_2\)

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 C\(_2\)H\(_2\) 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 \( (A^2\Sigma^+) + C_2H_2 \) 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 C\(_2\)H\(_2\). 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 C\(_2\)H\(_2\) cause C\(_2\)H\(_2\) to isomerize into its \textit{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 C\(_2\)H\(_2\) play in the electronic quenching of NO \( (A^2\Sigma^+) \) by C\(_2\)H\(_2\). Our work informs future velocity-map imaging experiments and non-adiabatic dynamics simulations on this system.