EXPLORING THE MECHANISM OF THE ELECTRONIC QUENCHING OF NO ($A^2\Sigma^+$) WITH CO_2

AERIAL BRIDGERS, ANDREW S. PETIT, *Department of Chemistry, California State University, Fullerton, Fullerton, CA, USA*.

As a reactive radical species, NO has the potential to interact with other atmospheric molecules in unique ways. The method of experimental quantification, laser-induced fluorescence (LIF), measures NO along its $A^2\Sigma^+ \leftarrow X^2\Pi$ transition band. The electronic quenching of NO ($A^2\Sigma^+$) through interactions with other molecules provides alternate photochemical pathways that compete with fluorescence. Previous experimental studies demonstrated that the room temperature electronic quenching cross section of the NO ($A^2\Sigma^+$)+CO_2 system is quite large at 64 $Å^2$. Recent experimental work by Paci et al. demonstrated that NO ($A^2\Sigma^+$)+CO_2 electronic quenching is accompanied by the formation of vibrationally excited CO_2 in its asymmetric stretching mode. However, the specific photochemical pathways responsible for this have not been identified.

In this work, we develop potential energy surfaces (PESs) to identify the photochemical pathways for the electronic quenching of NO ($A^2\Sigma^+$) by CO_2. The PESs are calculated at the EOM-EA-CCSD/d-aug-cc-pVTZ//EOM-EA-CCSD/aug-cc-pVDZ level of theory. This method is well-suited for open-shell systems and provides a balanced treatment of valence and Rydberg states. Long-range interactions between the N of NO ($A^2\Sigma^+$) and the O of CO_2 are attractive, causing the two molecules to move closer together. As the intermolecular distance decreases, electronic density shifts from the 3sσ orbital of NO ($A^2\Sigma^+$) to a 2pπ^* orbital of CO_2. This phenomenon, known as the harpoon mechanism, causes increased intermolecular attractions, distortion of CO_2 into a bent conformation, and a downhill pathway to a conical intersection. Overall, our work gives new insights into the chemical physics of an atmospherically relevant system that will inform future velocity map imaging experiments.