IMAGING THE ELECTRONIC QUENCHING DYNAMICS OF NITRIC OXIDE WITH MOLECULAR COLLISIONAL PARTNERS

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Abstract: Nitric oxide (NO) radicals are a common reactive intermediates and byproducts of incomplete combustion of fossil fuels, are present in the atmosphere and interstellar medium, and are an important contributor to urban smog. Using high-level theoretical calculations, I investigated the probability that NO would be electronically quenched from its excited state via collisions with H_2 and N_2. For H_2, we found that all interactions were repulsive with no quenching predicted. However, collisions with N_2 showed that for nitrogen-first orientations, NO underwent electronic quenching with the lowest barrier to interaction at 111 degrees.

Introduction

Nitric oxide (NO) radicals are reactive intermediates in combustion and in the atmosphere that contribute to smog. NO is produced through incomplete combustion, is an important contributor to acid rain and smog and a notable fragment from the photodissociation of aromatic chromophores implicated in 'brown carbon' aerosols with nitro functional groups.[1] NO has impacts on human health, as it can trigger aerosol formation of particulate matter below 2.5 microns, along with reacting to form tropospheric ozone.[2,3] Understanding NO energy transfer mechanisms in turbulent flows, like those created from high-speed flight, will aid improvements of future aerospace technologies. Furthermore, this will also enhance our understanding of atmospheric chemical processes, such as the reaction pathways of NO, which are essential for chemical modeling of NO_x emissions.

The concentration of NO is monitored in the atmosphere through its well-characterized absorption band system ($X^2\Pi \rightarrow A^2\Sigma^+$), commonly using fluorescence. Accurate measurements of NO concentrations rely on precise fluorescence quantum yields, which are hindered by electronic quenching (or collisional deexcitation) of NO ($A^2\Sigma^+$) with ambient molecular species such as oxygen (O_2) as shown in Figure 1.[1] In combustion and atmospheric environments, NO may undergo electronic quenching with nearby colliding molecules and atoms allowing for energy transfer to different electronic, vibrational, rotational degrees of freedom.

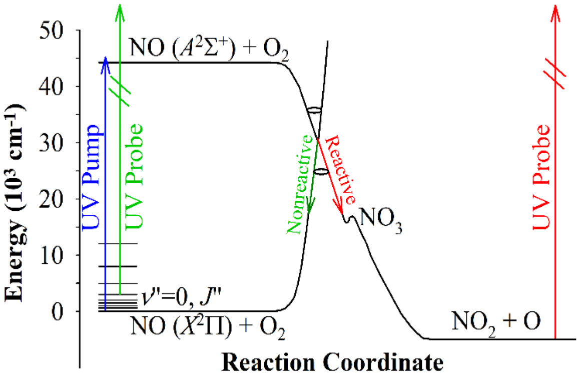

Figure 1: *Reaction coordinate diagram for NO with O_2 showing both the reactive and non-reactive quenching pathways.*

Better understanding of the fundamental intermolecular interactions of laser excited NO with H_2 and N_2 will help reveal the quenching dynamics of NO in both stellar and atmospheric environments. Indeed, H_2 is the most abundant molecule in the universe, with NO also present in nebula molecular clouds, and N_2 is the most abundant molecule in Earth's atmosphere. NO with H_2 serves as a model three-atom system and helps characterize the electronic quenching of NO by σ-bonding systems. N_2 provides an interesting comparison for my prior work with O_2, as they are both π-bonding systems, with N_2 elucidating the closed shell system analog to the O_2 open shell system. Furthermore, my studies will be of practical importance in precise turbulence modeling in hypersonic flows, which relies upon accurate accounting for electronic quenching.[4] This aligns with Thrust 3 of NASA's Aeronautics Research Mission Directorate.

Electronic quenching occurs when a high-energy molecule has its excited state population deactivated via collisional interactions, which may undergo two pathways: reactive and nonreactive electronic quenching as seen in Figure 1. Reactive quenching occurs when the energy lost from the excited species is partitioned into the breaking and formation of chemical bonds. In the case of NO with O_2, the formation of new products such as NO_2 and O-atoms would be observed under reactive quenching. Energy exchange between the NO and the collision partner is a signature from nonreactive quenching, with energy partitioned into translation, rotation, vibration and/or electronic modes, with NO returned to its ground electronic state. For collision partners with electronic states available between the ground and excited state of NO, energy exchange to rovibrational modes is likely. However, for collision partners with low-lying electronic states, electronic activation of the collision partner, in addition to rovibrational excitation, is plausible.[1]

Systems like NO+H_2 and N_2 are amenable to rigorous theoretical calculations to generate accurate potential energy surfaces (PES), using experimental results to refine them and yield insights into the basic forces acting upon nuclei during electronic quenching.

Methods

Stationary points on several electronic states of NO, relevant to our laser experimental work, were calculated using the Q-Chem 5.3 software[5] to determine the energetics and IQmol 2.15 for analysis of results. Our interests lie in mapping the potential energy surfaces (PESs) of NO with various molecular partners to predict the likelihood of reactive and nonreactive electronic quenching with H_2 and N_2. To this end, PESs were obtained from scanning bond angle θ_{ONN} and torsional angle θ_{ONNN}. See appendix for full list of geometries surveyed. NO with H_2 and N_2 using the electron attachment variant of equation of motion coupled cluster theory (EOM-EA-CCSD) with an aug-cc-pVDZ basis. EOM-EA-CCSD balances treatment of valence electrons and Rydberg electronic states of radicals with a single unpaired electron. We found that a singly excited determinant corresponding to adding an electron to the closed shell reference (NO^+) described the excited states well. Total contribution of doubly excited determinants, which correspond to exiting an electron in the NO^+ cation and adding an electron to the cation, was below 10% for all excited states. The calculated electronic adiabatic energy gap calculated at the EOM-EA-CCSD//aug-cc-pVDZ level of theory, 5.31 eV, is within 0.14 eV of the experimental value, 5.45 eV.

To validate this approach, we compared it to values in the literature on NO ($X\ ^2\Pi_{1/2}$) and NO ($A\ ^2\Sigma^+$ 3sσ). The optimized N-O bond lengths were found to be 1.16 Å and 1.07 Å for NO ($X\ ^2\Pi_{1/2}$) and NO ($A\ ^2\Sigma^+$ 3sσ), respectively, and were within 0.01 Å of the experimental values of 1.15 Å and 1.06 Å.

For the near exhaustive geometries surveyed of NO with H_2 and N_2, each geometry originates from Cartesian coordinate files hand built in IQmol, with geometry optimized to NO's third excited state, a Rydberg excited state, and electronic energies calculated for NO's first 6 excited states. Geometric constraints on bond angle and torsion were added to ensure a diverse array of geometries was surveyed. Calculations were run using Q-Chem software on CSU Fullerton's Kepler and NSF's XSEDE computing clusters, and data analysis and mapping of PES from the points calculated along the PES of each geometry of the cluster in search of low energy conical intersections.

Results

Figure 2 and 3 show the adiabatic potential energy curves for the lowest 6 electronic states of NO with H_2 and N_2, respectively, as a function of the intermolecular distance (R) between NO and the molecular collision partner. For all geometries included in the figures, the angle (H_2: θ_{ONH}; N_2: θ_{ONN}) was constrained at 111° for calculations involving N_2 and at 120° for the H_2 calculations. The electronic states are labeled based on their electronic character in the asymptotic limit (e.g., R_{HN}=10.0 Å). The ground and spin-orbit excited states of NO are D_0 ($X\ ^2\Pi_{1/2}$) and D_1 ($X\ ^2\Pi_{3/2}$), respectively, which are degenerate in our calculations at large R since spin-orbit coupling was not included. Furthermore, D_2 ($A\ ^2\Sigma^+$ 3sσ) is the s Rydberg state of NO largely built from the 3s atomic orbitals, while D_3 ($C\ ^2\Pi_{1/2}$) and D_4 ($C\ ^2\Pi_{3/2}$) are π Rydberg states. Additionally, D_5 ($D\ ^2\Sigma^+$ 3ps) is a s Rydberg state that is largely built from the 3p atomic orbitals. All energies are reported in electron volts (eV) relative to the energy at the D_2 optimized geometry with the NO and molecular collision partners constrained to be 10.0 Å apart.

As illustrated in Figure 2, the potential energy surfaces for θ_{ONH} = 120° are repulsive with respect to the intermolecular distance between NO and H_2 (R_{NH}). Furthermore, the adiabatic surfaces do not cross at any point, signifying the absence of any conical intersections at low energies. As a result, NO ($A^2\Sigma^+$) is predicted to not undergo reactive or nonreactive electronic quenching with H_2 under low collision energies.

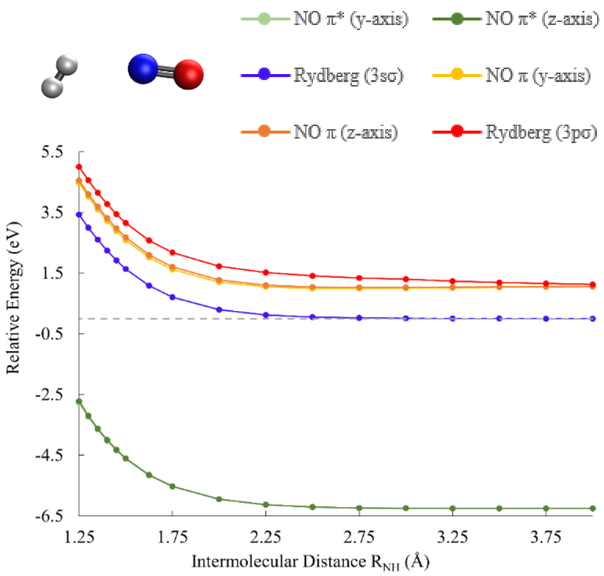

Figure 2: *Adiabatic potential energy curves of the first 6 electronic states for NO+H_2 as a function of the distance between N and H (R_{NH}) at a fixed O-N-H angle (θ_{ONH}) of 120°; all other geometric parameters were optimized on D_2 ($A\ ^2S^+$ 3sσ).*

Figure 3 shows the corresponding adiabatic potential energy curves for NO with N_2 for θ_{ONN} = 111°. Here, the calculated surfaces show striking differences compared to H_2. As the intermolecular distance (R_{NN}) decreases, the D_2, D_3, and D_4 potential energy surfaces become closer in energy to each other. In particular, the D_3 ($C\ ^2\Pi_{1/2}$) and D_4 ($C\ ^2\Pi_{3/2}$) π Rydberg states decrease in energy at similar rates as a function of R_{NN}. The D_2 ($A\ ^2\Sigma^+$ 3sσ) surface at large R_{NN} distance is relatively flat but reaches a barrier of 0.404 eV at R_{NN} = 2.25 Å. The D_2 and D_3 potential energy curves also approach each other in the vicinity of this barrier on D_2. At even smaller R_{NN} distances, the energy of the D_2 potential energy curve decreases in energy until it reaches a conical intersection with D_1 at approximately R_{NN} = 1.66 Å and 0.239 eV.

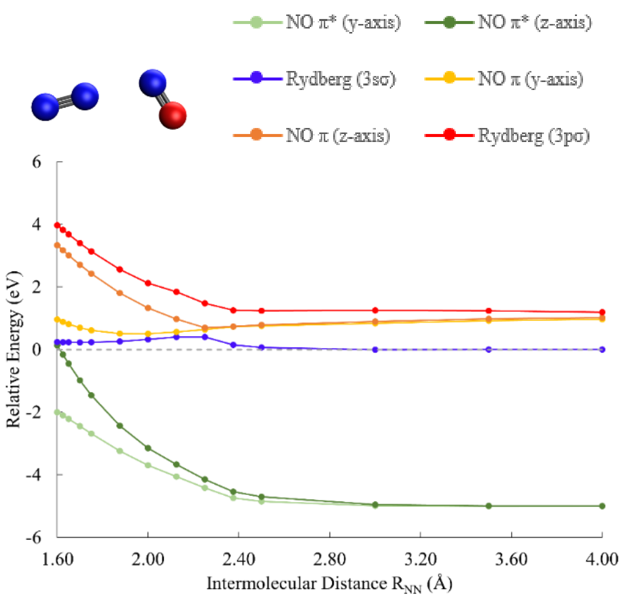

***Figure 3:** Adiabatic potential energy curves of the first 6 electronic states for $NO+N_2$ as a function of the distance between N and N (R_{NN}) at a fixed O-N-N angle (θ_{ONN}) of 111°; all other geometric parameters were optimized on D_2 ($A\ ^2S^+$ 3sσ).*

Discussion

For $NO+H_2$, for all geometries surveyed interactions were found to be repulsive. The molecules did not form a conical intersection, moving consistent to a repulsive wall, which indicated that no electronic quenching of excited NO would occur.

Molecular nitrogen did exhibit geometry specific behavior which shows that orientation matters for which electronic quenching pathways are accessible; nitrogen first is the preferred pathway for state crossing, with a preference for interactions around 111 degrees. Based on analysis of orbital character in Figure 4, the Rydberg state (D_2) gains more π character. D_2 has interactions with NO's π and π* orbitals (D_1 and D_3). These interactions imply there are quenching interactions with N_2 through a conical intersection in π orbital overlap that occurs around 111 degrees. Low energy geometries occurred with azide (N=N=N) like shapes being formed. These quenching interactions were observed over a bond angle (θ_{ONN}) of 90 to 135, the lowest barrier at 111. The strong quenching interaction that occurs around 111 degrees for the nitrogen of NO as a vertex shows that N_2 is a strong non-reactive quencher of NO.

It was noticed that there were changes in the character of D_2 states for $NO+N_2$ to allow symmetry of NO Rydberg to match that of the LUMO of NO's π^* (D_3) as shown in Figure 4.

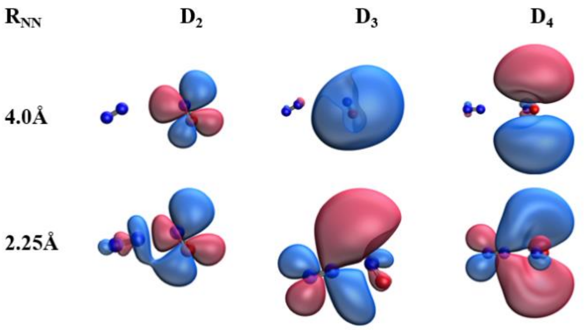

***Figure 4**: Singly occupied molecular orbitals (SOMOs) for the D_2 through D_4 states of $NO+N_2$ with θ_{ONN}=111° and R_{NN}=2.13 Å and R_{NN}=4.00 Å. Note that the state with 3sσ character changes from D_2 when R_{NN}=4.00 Å to D_4 at R_{NN}=2.13 Å. Different orientations of view are used to better highlight the shapes of the SOMOs. The calculations were performed at the EOM-EA-CCSD/aug-cc-pVDZ level of theory and the SOMOs are plotted with an isovalue of 0.040.*

Conclusion

We launched this investigation in search of the specific geometries favored for non-reactive quenching pathways of NO ($A^2\Sigma^+$) by molecular hydrogen and nitrogen. We were selective in choosing our level of theory (EOM-EA-CCSD) for the computational analysis. This level of theory was selected for its ability to handle the complex nature of simulating electron behavior and energetics of open-shelled radicals. Using NO^+ as a reference and then attaching on an electron, eliminates the open-shell conundrum since only one electron need be handled by the models. Because NO is experimentally excited into the Rydberg ($A^2\Sigma^+$ 3sσ) state, here identified as D_2, it is only necessary to ensure the basis set is large enough for accurate calculations to be completed. For our geometric optimizations, we used aug-cc-pVDZ. After a plethora of attempts, only a few orientations demonstrated to be promising. Our results indicate that quenching by N_2 may occur only when the nitrogen atom of NO is aligned with a nitrogen of N_2 at angles between 90° and 135°.

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References

1. Blackshaw, K. J. *et al.* Imaging the nonreactive collisional quenching dynamics of NO (A 2 Σ+) radicals with O 2 (X 3 Σ g −). *J. Chem. Phys.* **151**, 104304 (2019).
2. Bange, H. W. Gaseous Nitrogen Compounds (NO, N2O, N2, NH3) in the Ocean. in *Nitrogen in the Marine Environment* 51–94 (2008). doi:10.1016/B978-0-12-372522-6.00002-5
3. Fassina, V. Air Pollution in Relation to Stone Decay. in 111–179 (2020).
4. Sánchez-González, R., Bowersox, R. D., & North, S. W. Simultaneous velocity and temperature measurements in gaseous flowfields using the vibrationally excited nitric oxide monitoring technique : a comprehensive study. *Appl. Opt.* **51**, 1216–1228 (2012).
5. Shao, Y. *et al.* Advances in molecular quantum chemistry contained in the Q-Chem 4 program package. *Mol. Phys.* **113**, 184–215 (2015).

Appendix

For NO+H_2, both nitrogen and oxygen-first orientations, numerous bond angles were sampled. Potential energy surfaces were mapped for bond angles of 90, 120, 150 and 180, and torsional angles of 0 and 90. For NO+N_2, both nitrogen and oxygen-first orientations, potential energy surfaces were mapped for bond angles of 90, 105, 120, 150 and 180 degrees, and torsional angles of 0, 90 and 180 degrees. For nitrogen-first orientations, bonds angles of 111, 115 and 135 were also mapped.

Figure 5 and 6 show the adiabatic potential energy surfaces of NO with H_2 and N_2 for the first 6 electronic states for oxygen first configurations at the same angles at the nitrogen figure above (Figure 2 and 3). These surfaces clearly show that oxygen first interactions are significantly less favored and are quite repulsive in nature.

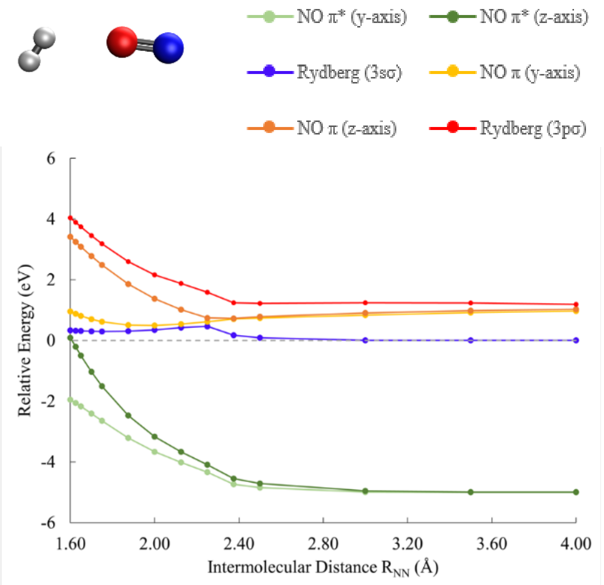

Figure 5: *Adiabatic potential energy curves of the first 6 electronic states for NO+H_2 as a function of the distance between N and H (R_{NH}) at a fixed N-O-H angle (θ_{NOH}) of 120°; all other geometric parameters were optimized on D_2 (A $^2\Sigma^+$ 3sσ).*

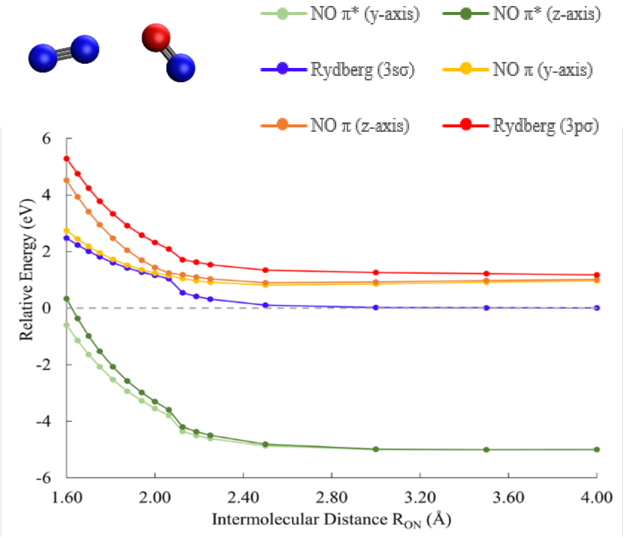

Figure 6: *Adiabatic potential energy curves of the first 6 electronic states for* $NO+N_2$ *as a function of the distance between O and N* (R_{NN}) *at a fixed N-O-N angle* (θ_{NON}) *of 120°; all other geometric parameters were optimized on* D_2 ($A\ ^2\Sigma^+\ 3s\sigma$).