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Reactive Quenching of NO (A^2Σ^+) with H_2O Leads to HONO: A Theoretical Analysis of the Reactive and Nonreactive Electronic Quenching Mechanisms

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Abstract

The electronic quenching of NO (A^2Σ^+) with molecular partners exemplifies the rich non-adiabatic dynamics that occurs on multiple, coupled potential energy surfaces (PESs). The mechanistic details of the electronic quenching depend sensitively on the nature and strength of the intermolecular interactions between NO (A^2Σ^+) and the molecular partner. In this paper, we reveal the electronic quenching mechanisms of NO (A^2Σ^+) with H_2O, a non-adiabatic process with an extremely large cross section of 121 Å^2 near room temperature. In doing so, we demonstrate that the NO (A^2Σ^+)+H_2O PES funnels a wide range of initial intermolecular orientations to the same minimum-energy geometry. Furthermore, we reveal low-energy pathways to conical intersections between NO (A^2Σ^+)+H_2O and NO (X^2Π)+H_2O that primarily involve decreasing the intermolecular distance and elongating a single O-H bond of H_2O. Based on these geometric distortions, we predict that nonreactive electronic quenching will be associated with significant vibrational excitation in a local O-H stretch mode in H_2O. Reactive quenching will produce a H-atom and HONO, an important intermediate in atmospheric and combustion chemistry and a precursor to the hydroxyl radical. Overall, our work provides the first detailed theoretical study of the mechanism of the electronic quenching of NO (A^2Σ^+) with a polyatomic molecular partner, as well as makes concrete predictions to inform future velocity map imaging experiments.
Introduction

Laser-induced fluorescence (LIF) on the \(A^2\Sigma^+ \leftarrow X^2\Pi\) transition band is a well-established tool used to quantify nitric oxide (NO) concentrations in the atmosphere and operating combustion engines.\(^1\)–\(^4\) However, molecules and atoms present in these environments interfere with the LIF quantification of NO through electronic quenching. In electronic quenching, collisions between NO \((A^2\Sigma^+)\) and an atomic or molecular partner provide nonradiative pathways back to the electronic ground state that compete with fluorescence. In fact, depending on the collisional partner, electronic quenching can dominate over fluorescence.\(^5\)--\(^7\) Therefore, electronic quenching may strongly affect the measured LIF intensities, leading to an underestimate of the true NO concentration.

To correct for inaccuracies in the determination of NO concentrations from LIF measurements, electronic quenching cross sections of known collisional partners have been experimentally measured.\(^6\)--\(^10\) Settersten and co-workers reported experimentally determined electronic quenching cross sections of NO \((A^2\Sigma^+)\) with different collisional partners at various temperatures. Table 1 shows that NO \((A^2\Sigma^+)+\text{H}_2\text{O}\) has an electronic quenching cross section of 121 Å\(^2\) at 294 K.\(^9\) This is significantly larger than the electronic quenching cross sections of NO \((A^2\Sigma^+)\) with N\(_2\), CO, and O\(_2\) at 294 K: 0.007 Å\(^2\), 6.55 Å\(^2\), and 28.5 Å\(^2\), respectively.\(^10\) Additionally, Table 1 shows that the electronic quenching cross section of the NO \((A^2\Sigma^+)+\text{N}_2\) system increases as the temperature is increased above 294 K, that is, \(\frac{d\sigma}{dT}\bigg|_{T=294\ K} > 0\). In contrast, \(\frac{d\sigma}{dT}\bigg|_{T=294\ K} < 0\) for the other molecular partners. This suggests that electronic quenching in these systems proceeds through a NO \((A^2\Sigma^+)\)+M collision complex whose formation is more likely at lower temperatures.\(^9\)\(^,\)\(^10\) While experimental electronic quenching cross sections are useful to correct the LIF measurements of NO \((A^2\Sigma^+)\), the underlying photochemical mechanisms responsible for
electronic quenching are still not well understood.

Table 1. Experimentally determined electronic quenching cross sections of NO ($A^2Σ^+$) with the Molecular Partners $N_2$, CO, $O_2$, and $H_2O$.

| Molecular Partner | Electronic Quenching Cross Section (σ) at 294 K | Sign of $\frac{dσ}{dT}|_{T=294\,K}$ |
|-------------------|-----------------------------------------------|-------------------------------------|
| $N_2$             | 0.007 Å$^2$                                   | $>0$                                |
| CO                | 6.55 Å$^2$                                    | $<0$                                |
| $O_2$             | 28.5 Å$^2$                                    | $<0$                                |
| $H_2O$            | 121 Å$^2$                                     | $<0$                                |

Using NO ($A^2Σ^+$)+$H_2O$ as an example, collisions between NO ($A^2Σ^+$) and $H_2O$ can result in three different classes of energy-exchange pathways:

1. $\text{NO} \left( A^2Σ^+, v_i, J_i \right) + H_2O \left( X^1A_1, v_{f,2}, J_{f,2} \right) \rightarrow \text{NO} \left( A^2Σ^+, v_f, J_f \right) + H_2O \left( X^1A_1, v_{f,2}, J_{f,2} \right)$
2. $\text{NO} \left( A^2Σ^+ \right) + H_2O \rightarrow \text{NO} \left( X^2Π \right) + H_2O$
3. $\text{NO} \left( A^2Σ^+ \right) + H_2O \rightarrow HONO + H$

The first channel represents an inelastic collision in which energy is exchanged among the rovibrational levels of NO ($A^2Σ^+$) and $H_2O$; NO remains in its $A^2Σ^+$ excited electronic state. The second channel is an example of nonreactive electronic quenching resulting in a nonradiative NO ($A^2Σ^+$) → NO ($X^2Π$) transition, with the released energy partitioned among the nuclear degrees of freedom of the two molecules and relative translation. Because the lowest energy excited electronic state of $H_2O$ lies above NO ($A^2Σ^+$), collisions between NO ($A^2Σ^+$) and $H_2O$ cannot electronically excite the $H_2O$ molecule. Lastly, the third channel exhibits reactive electronic quenching, in which the electronic excitation induces a chemical reaction. Channels 2 and 3 occur via conical intersections that couple the excited and ground electronic states of the NO-$H_2O$ quenching pair.
A number of previous studies have focused on determining the underlying photochemical mechanisms of the electronic quenching of NO \((A^2\Sigma^+)\) with atomic and molecular partners. The majority of these have focused on the collision channels of NO \((A^2\Sigma^+)\) with rare gas atoms.\(^{11-15}\) Studies involving molecular partners have primarily focused on the inelastic scattering channel (Equation 1). For example, Luxford and co-workers studied inelastic collisions between NO \((A^2\Sigma^+)\) and \(D_2\).\(^{13}\) Their work demonstrated that the NO \((A^2\Sigma^+)\)+D\(_2\) PES is similar to that of NO \((A^2\Sigma^+)\)+He but rotational energy transfer between NO \((A^2\Sigma^+)\) and \(D_2\) produces more anisotropic NO fragments than what is observed in NO \((A^2\Sigma^+)\)+He.\(^{13}\) In a theoretical study on the same system, Pajón-Suárez and co-workers developed an interaction PES for NO \((A^2\Sigma^+)\)+H\(_2\) over intermolecular distances ranging from 5–10 Å and showed that it was comparable to the interaction PES of NO \((A^2\Sigma^+)\) with rare gas atoms.\(^{16}\) In another experimental study, Luxford and co-workers utilized crossed molecular beams to probe inelastic rotational energy transfer in collisions between NO \((A^2\Sigma^+)\) and \(N_2\).\(^{17}\) Their study revealed insights into the stereodynamics of the rotational energy transfer, with a clear preference for a linear ON−N\(_2\) complex on the ON \((A^2\Sigma^+)\)−N\(_2\) PES with the N-atom of NO pointing toward N\(_2\). More recently, Parsons and co-workers used velocity map imaging (VMI) to characterize the translational kinetic energy and NO \((A^2\Sigma^+)\) rotational state distributions associated with the photodissociation of the NO+N\(_2\) complex.\(^{18-20}\) Finally, Soulié and Paterson recently published a NO \((A^2\Sigma^+)\)+O\(_2\) \((X^3\Sigma_g^-)\) van der Waals PES, which contains a collision complex in an O-N-O-O-O linear geometry with an intermolecular distance of 4.3 Å and a binding energy of 95 cm\(^{-1}\).\(^{21}\)

Three recent studies on NO \((A^2\Sigma^+)\)+O\(_2\) are among the few that directly probe the mechanism of nonreactive electronic quenching of NO \((A^2\Sigma^+)\) with a molecular partner. In the first, Few and co-workers used time-resolved Fourier-transform infrared emission spectroscopy to
measure vibrationally excited NO (X^2Π, ν′′=2–22) produced through nonreactive electronic quenching.\textsuperscript{22} They observed a bimodal distribution which implied the presence of two channels. The first channel involves the production of NO (X^2Π) generated with high ν′′, along with O\textsubscript{2} co-products made in its X^3Π\textsubscript{g} or a^1Δ\textsubscript{g} electronic state. The authors speculated that NO (X^2Π) produced with low ν′′ are formed from a second channel, which involves either the generation of O\textsubscript{2} (e^1Σ\textsubscript{u}⁻) via a harpoon mechanism or the formation of O\textsubscript{2} (X^3Π\textsubscript{g}) through an inefficient process. More recently, Blackshaw and co-workers used VMI to determine the quantum-state resolved dynamical mechanisms of NO (A^2Σ\textsuperscript{+})+O\textsubscript{2} nonreactive electronic quenching to NO (X^2Π, ν′′=0) products.\textsuperscript{23} In this study, the relatively low total kinetic energy release (TKER) to products suggests that a significant fraction of the available energy is partitioned into the electronic, vibrational, and rotational levels of O\textsubscript{2}. Phase space theory simulations of the TKER distribution show good agreement with the experimental data when O\textsubscript{2} is taken to be formed in its O\textsubscript{2} (e^1Σ\textsubscript{u}⁻) excited electronic state. As such, the outcomes from this nonreactive electronic quenching channel are consistent with the majority of the available energy ultimately ending up driving the electronic excitation of O\textsubscript{2}. A recent theoretical study by Soulié and Paterson used multireference methods, SA-CASSCF and XMS-CASPT2, to develop a mechanistic rationalization of these experimental observations.\textsuperscript{24} They identified two electronic quenching pathways, with the first proceeding via a transient ion-pair created by electron transfer from NO (A^2Σ\textsuperscript{+}) to O\textsubscript{2} and the second requiring significant elongation of the O\textsubscript{2} bond length. Soulié and Paterson argued that the first pathway exhibits a stronger dependence on the intermolecular orientation than the second. Moreover, the first pathway is predicted to produce greater vibrational excitation in the products due to the large geometric changes caused by the transient electron transfer.
Turning to the reactive electronic quenching pathway, Umemoto and co-workers experimentally probed the production of H atoms from collisions of NO (A\(^2\Sigma^+\)) with H\(_2\)O, C\(_2\)H\(_5\), and C\(_2\)H\(_4\).\(^{25}\) In their experiments, a pump pulse excited the NO A\(^2\Sigma^+\) ← X\(^2\Pi\) band while a probe pulse monitored the formation of H-atoms via excitation to the 2\(^2\)S state. The electronically excited H atoms then underwent collisional relaxation to the 2\(^2\)P state which ultimately fluoresces in the vacuum ultraviolet, allowing for their detection. Analysis of the Doppler profile of the H-atom 2\(^2\)P→1\(^2\)S fluorescence signal suggested that a large fraction of the available energy, approximately 47.5% for NO (A\(^2\Sigma^+\)) + H\(_2\)O, is partitioned into translational kinetic energy. These observations suggested that the reactive electronic quenching process involves a short-lived collision complex. The authors speculated, as in Equation 3, that the reactive electronic quenching of NO (A\(^2\Sigma^+\)) with H\(_2\)O results in HONO formation. HONO plays a crucial atmospheric role in air quality, making the photochemistry of NO (A\(^2\Sigma^+\)) + H\(_2\)O of potential importance in atmospheric chemistry.\(^{26}\) Umemoto and co-workers additionally reported CASSCF calculations performed on the NO+H\(_2\)O system in the C\(_s\) point group, which indicated that the lowest 2A' state, which we will denote as D\(_1\), adiabatically correlates to both the NO (X\(^2\Pi\))+H\(_2\)O (X\(^1\)A\(_1\)) and H (\(^2\)S)+HONO (\(^1\)A') product channels. This provides further support for HONO formation in the reactive electronic quenching process.

Outside of electronic quenching, several experimental and computational studies have focused on the NO+H\(_2\)O system. Lacome and co-workers performed experimental IR spectroscopy studies of NO+H\(_2\)O, NO+HDO, and NO+D\(_2\)O in a solid neon matrix.\(^{27}\) Analysis of these spectra, along with electronic structure calculations performed at the B3LYP/6-311++G(2d,2p) level of theory, indicated that the most stable NO+H\(_2\)O complex geometry involves the nitrogen atom of NO hydrogen-bonding with H\(_2\)O. Salmi and co-workers obtained optimized geometries for
NO+H₂O in both its ²A' and ²A'' states (D₀ and D₁) at the CCSD(T)/A'VQZ level of theory.²⁸ They identified two ²A’ hydrogen-bonding conformers as well as two ²A'' electron donor-accepter complexes in which the oxygen atom of H₂O interacts with the nitrogen atom of NO; all four of these conformers are within 0.13 kcal/mol of each other. Additionally, Salmi and co-workers modeled the O-H stretching and H-O-H bending regions of the vibrational spectra of the NO+H₂O conformers as well as the N-O stretching vibronic transitions of the A²Σ⁺ ←X²Π band. Finally, several additional theoretical studies have attempted to develop insights into the physical origin of the intermolecular interactions in the NO+H₂O complex, as well as map out the D₀ and D₁ PESs.²⁹–³¹ Outside of the CASSCF calculations reported by Umemoto and co-workers, the photochemistry of NO (A²Σ⁺)+H₂O has not yet been explored.

Given the dearth of knowledge about the photochemical mechanisms responsible for NO (A²Σ⁺) electronic quenching with molecular partners, we recently performed a detailed theoretical study of the NO + H₂, NO + N₂, and NO + CO systems.³² Figure 1 shows PESs calculated at the EOM-EA-CCSD/d-aug-cc-pVTZ//EOM-EA-CCSD/aug-cc-pVDZ level of theory for the D₂ (NO (A²Σ⁺)+M) and D₁ (NO (X²Π)+M) states, where M is the collision partner, as a function of the intermolecular distance. The states are identified based on their electronic character at the asymptotic limit when NO+M are 10 Å apart. For each complex, the intermolecular orientation was constrained to a value that we previously identified to be most favorable for electronic quenching: θₜₐₜ₉ = 120° for ON+CO, θₙₕₜ₉ = 111° for ON+N₂, and θₜ₉ₙ = 111° for ON+H₂.
Figure 1. Cuts of the adiabatic PESs for the D$_1$ (dashed lines) and D$_2$ (solid lines) electronic states of the complexes ON+CO (blue lines), ON + N$_2$ (red lines), and ON + H$_2$ (black lines) along the intermolecular distance. All electronic energies are reported relative to NO ($A^2\Sigma^+$) + M at R=10 Å. Only the NO ($A^2\Sigma^+$) + CO system exhibits a downhill pathway to a D$_2$-D$_1$ conical intersection, which facilitates electronic quenching at low thermal energies. For further details, see our previous paper.\textsuperscript{32}

The cuts of the PESs shown in Figure 1 reveal clear differences between the three systems, which reflect their experimental electronic quenching cross sections, as well as make predictions for future velocity map imaging (VMI) studies. While the D$_1$ PES is repulsive for all three systems, the D$_2$ PES is very different for each molecular partner. In particular, H$_2$ was the only molecular partner that showed no evidence of a conical intersection between D$_2$ and D$_1$ that would facilitate electronic quenching because both PESs are purely repulsive. Rather, it was predicted that inelastic scattering would be the primary deactivation mechanism for NO ($A^2\Sigma^+$) collisions with H$_2$. Although a D$_2$-D$_1$ conical intersection is formed for NO+N$_2$, it can only be reached if the colliding
molecules overcome a barrier of 0.404 eV. This suggests that there is a low probability for electronic quenching at low temperatures because the barrier will cause the internal conversion kinetics to be slower than the fluorescence rate of NO (A^2Σ^+); the approximate radiative lifetime of NO (A^2Σ^+) is 193 ns.\textsuperscript{23} We posit that the NO (A^2Σ^+) + N\textsubscript{2} electronic quenching cross section increases from 0.007 Å\textsuperscript{2} at 294 K to 0.116 Å\textsuperscript{2} at 765 K due to the colliding molecules having greater thermal energy to surmount the barrier.\textsuperscript{9} In contrast, NO (A^2Σ^+) has a higher electronic quenching cross section with CO because the D\textsubscript{2} PES has no barrier preceding the D\textsubscript{2}-D\textsubscript{1} conical intersection. Moreover, this conical intersection lies below the asymptotic limit where the intermolecular interactions are attractive. Our data, therefore, explains why CO facilitates significantly greater electronic quenching of NO (A^2Σ^+) near room temperature than H\textsubscript{2} or N\textsubscript{2}, which is reflected by the experimental cross section of 6.55 Å\textsuperscript{2} at 294 K.

Figure 2 provides a more detailed description of the ON + CO PESs, with the six lowest-energy electronic states shown as a function of the intermolecular distance, \( R_{CN} \), and a fixed intermolecular orientation of \( \theta_{CNO} = 120° \). The D\textsubscript{2} PES exhibits weak long-range attraction. Close to \( R_{CN}=2.50 \) Å, we see a drastic increase in the strength of the attractive intermolecular interactions on D\textsubscript{2} that funnels the colliding molecules into a D\textsubscript{2}-D\textsubscript{1} conical intersection that lies well below the asymptotic limit. Further investigations led us to determine that the NO+CO PESs are significantly anisotropic, with only a narrow range of intermolecular orientations consistent with a downhill pathway to a D\textsubscript{2}-D\textsubscript{1} conical intersection. Moreover, the D\textsubscript{2} PES is only very weakly attractive at intermolecular distances greater than 2.75 Å and is hence only able to guide the colliding molecules into the orientations that can reach the D\textsubscript{2}-D\textsubscript{1} conical intersections when their translational and rotational energies are low. This is consistent with the experimental observation
that the NO \( (A^2\Sigma^+)+\) CO electronic quenching cross section increases from 6.55 Å² at 294 K to 13.6 Å² at 125 K.\(^9,10\)

Figure 2. Cuts of the adiabatic PESs of the first six electronic states for ON + CO as a function of the distance between N and C \( (R_{CN}) \) at a fixed C−N−O angle \( (\theta_{CNO}) \) of 120°; the remaining geometric parameters were optimized on D\(_2\). The states are labeled based on their electronic character at \( R_{CN} = 10.0 \) Å, and all energies are reported relative to that of D\(_2\) at \( R_{CN} = 10.0 \) Å. Around \( R_{CN}=2.50 \) Å, the strength of the intermolecular attractions on D\(_2\) significantly increases, and the D\(_2\) PES funnels population to the D\(_2\)-D\(_1\) conical intersection. Additionally, note the apparent avoided crossing between D\(_2\) and D\(_4\) near \( R_{CN}=2.50 \) Å. For further details, see our previous paper.\(^32\)

Figure 2 demonstrates that the electronic quenching of NO \( (A^2\Sigma^+) +\) CO is facilitated by the dramatic increase in intermolecular attractions below \( R_{CN}=2.50 \) Å. We attributed this to a harpoon mechanism, in which electron density shifts from the NO \( (A^2\Sigma^+) \) Rydberg orbital to the CO \( \pi^* \) antibonding orbital, creating a transient ion pair that experiences Coulombic attractions.\(^8,32–35\)

The evidence for this is summarized in Figure 3. Panel 3A shows that as the two molecules move closer together, the electron spin density shifts from being localized on NO to being primarily
localized on CO. Similarly, panel 3B shows the development of significant partial positive charge on NO and partial negative charge on CO as $R_{CN}$ is reduced. Importantly, the most significant redistribution of charge and spin density occurs between $R_{CN} = 2.75 \, \text{Å}$ and $R_{CN} = 2.50 \, \text{Å}$, which is also the region where the $D_2$ PES becomes significantly attractive. The singly occupied molecular orbitals (SOMOs) shown in panel 3C provide additional support for a harpoon mechanism. At $R_{CN} = 4 \, \text{Å}$ the SOMO is mostly localized on NO and displays clear $3\sigma$ Rydberg character. As the intermolecular distance decreases, the SOMO develops greater amplitude on CO, eventually resembling the $2p\pi^*$ MO of CO with $3\pi$ Rydberg character on NO. This change in the electronic character of the $D_2$ state causes the development of bonding interactions between the two molecules and hence increased intermolecular attraction. In Figure 2, $D_2$ and $D_4$ appear to undergo an avoided crossing below $2.75 \, \text{Å}$. In that vicinity, the SOMOs show an exchange in electronic character between $D_2$ and $D_4$. As $D_2$ begins to express $3\pi$ Rydberg character, $D_4$ takes on $3\sigma$ Rydberg character.
Figure 3. Löwdin population analysis for the total spin densities (panel A) and partial charges (panel B) of NO and CO as a function of the distance between N and C ($R_{CN}$) beginning at a fixed C–N–O angle ($\theta_{CNO}$) of 120°. Panel C shows the SOMOs of D$_2$ at representative intermolecular distances. This analysis demonstrates that the increased intermolecular attraction between NO ($A^2\Sigma^+$) and CO on the D$_2$ PES, which occurs near $R_{CN}$=2.5 Å, is driven by electron transfer from NO to CO, i.e., a harpoon mechanism. For further details, see our previous paper.$^{32}$

In the present study, we apply the theoretical analysis exemplified in Figures 1-3 to the NO+H$_2$O system. In doing so, we develop a mechanistic analysis for the 20-fold greater electronic quenching cross section of NO ($A^2\Sigma^+$) with H$_2$O compared with CO at 294 K. Through our analysis, we identify clear pathways for both nonreactive and reactive electronic quenching. We additionally demonstrate that a harpoon mechanism is responsible for the long-range intermolecular attractions that steer the colliding NO ($A^2\Sigma^+$) and H$_2$O molecules into a region of the D$_2$ PES that facilitates quenching. Throughout, we make clear predictions about the outcomes of NO ($A^2\Sigma^+$)+H$_2$O electronic quenching that will inform future velocity map imaging experiments. In particular, we demonstrate that the nonreactive electronic quenching pathway
results in the formation of HONO, an important intermediate in atmospheric chemistry that serves as a major source of hydroxyl radicals, OH.

**Methods**

The equation-of-motion electron attachment coupled-cluster singles and doubles (EOM-EA-CCSD) method in conjunction with an aug-cc-pVDZ basis was used to perform the initial geometry optimizations; mechanistically important pathways were re-optimized using the EOM-EA-CCSD/aug-cc-pVTZ level of theory. EOM-EA-CCSD utilizes the closed-shell NO\(^+\)+H\(_2\)O reference to avoid the electronic structure challenges of using an open-shell NO+H\(_2\)O reference. This method accurately describes all target doublet states whose dominant electronic configurations can be built by adding an electron to a virtual orbital of the NO\(^+\)+H\(_2\)O reference. This is true regardless of whether the states are characterized as valence or Rydberg orbitals, as well as whether or not the states have significant charge-transfer character.\(^{36-38}\) The target states receive dynamic electron correlation through the inclusion of electron configurations that are doubly excited relative to the NO\(^+\)+H\(_2\)O reference. Single-point calculations were performed at the EOM-EA-CCSD/d-aug-cc-pVTZ level of theory. We specifically chose a doubly augmented basis set to provide a reliable description of the Rydberg excited states of interest. All calculated energies are reported relative to the optimized NO (A\(^2\Sigma^+\)) + H\(_2\)O complex constrained to have an intermolecular distance of 10 Å. Our chosen computational approach was carefully benchmarked and justified in our previous paper.\(^{32}\) In addition, in Figures S1-S3, we demonstrate that our approach provides the same overall mechanistic picture as the multireference method N-electron valence state perturbation theory (NVEPT2).\(^{39,40}\) Unless otherwise stated, all calculations were performed using Q-Chem 5.4 and analyzed using IQmol 2.15.\(^{41}\)

The EOM-EA-CCSD approach is known to be much less accurate for states with significant double excitation character.\(^{36,37}\) We verified that all of the states analyzed in this study
consistently have dominant single excitation character. Indeed, doubly excited determinants always contributed less than 10% to the electronic wave function for all the states. In particular, we verified that all states of interest retain dominant single excitation character throughout the reactive electronic quenching pathways, which, as discussed below, involve stretching an O-H bond of water.

To investigate the electronic properties of the excited states, we used natural transition orbitals (NTOs) that were visualized with wxMacMolPlt. Löwdin spin densities and partial charges were also investigated for all target states. To calculate both the NTOs and the Löwdin populations, we used the EOM-EA-CCSD/aug-cc-pVTZ level of theory.

**Results and Discussion**

Before mapping out cuts of the NO + H$_2$O PESs, we sought to identify the low-energy NO ($A^2\Sigma^+$) + H$_2$O collision complexes as well as to determine the degree of anisotropy in the asymptotic D$_2$ PES. We accomplished this by performing 272 unconstrained geometry optimizations that began in a wide variety of initial intermolecular orientations. We specifically explored NO-H$_2$O conformations in which the N or O atom of NO was oriented towards different sites of H$_2$O. For each overall arrangement, we varied the intermolecular orientation as well as sampled both planar and nonplanar geometries. For each starting geometry, the intermolecular distance was 3.50 Å.

The vast majority of the unconstrained geometry optimizations (242 out of 272) ultimately resulted in the same nonplanar collision complex with an intermolecular distance of $R_{ON} = 1.91$ Å and an energy of -0.57 eV relative to an optimized geometry on D$_2$ with $R_{ON} = 10$ Å. This nonplanar minimum-energy geometry is characterized by the NO lying above H$_2$O, the nitrogen of NO interacting with the oxygen of H$_2$O, and a H-O-N-O torsion angle of -178.6°; this ON-OH$_2$
collision complex is shown in the inset of Figure 4. Harmonic vibrational frequency analysis confirmed that this nonplanar geometry is a true minimum on the D$_2$ PES. While the majority of the 242 initial intermolecular orientations relaxed directly into the nonplanar collision complex, some led to low-energy saddle points with relative energies of -0.21 eV to -0.51 eV; all of these saddle points relaxed to the nonplanar collision complex after distorting along the imaginary frequency mode. These low-energy saddle points are primarily planar complexes or torsional conformers of the nonplanar collision complex.

The remaining 30 geometry optimizations can be classified into two groups. The first group, consisting of 23 geometry optimizations, relaxed into relatively high-energy saddle points with relative energies of -0.01 eV to 0.05 eV. Despite having high energies and significantly different geometries, all but one of these saddle points ultimately relaxed into the nonplanar collision complex discussed above after a geometric distortion along the imaginary frequency mode. The remaining 7 unconstrained geometry optimizations led to a nonplanar geometry where the oxygen of NO is directed towards the oxygen of H$_2$O with an intermolecular distance $R_{OO} = 2.34$ Å and a relative energy of -0.27 eV. Harmonic vibrational frequency analysis confirmed that this is a minimum on the D$_2$ PES. Analysis using the freezing string method and subsequent transition state geometry optimizations suggest that this local minimum re-arranges into the nonplanar ON-OH$_2$ collision complex with essentially no barrier.$^{44}$

Collectively, our analysis suggests that the NO ($A^2\Sigma^+$)+H$_2$O PES is effective at funneling a large variety of initial intermolecular orientations into the same minimum energy geometry. This is in sharp contrast to what we previously observed with NO ($A^2\Sigma^+$) and CO, where the D$_2$ PES is much more anisotropic and only a narrow range of initial intermolecular orientations facilitate electronic quenching. As will be discussed below, the propensity for a large fraction of collisions
between NO ($A^2\Sigma^+$) and H$_2$O to relax into the low-energy collision complex on the D$_2$ PES helps to explain why the electronic quenching cross section of NO ($A^2\Sigma^+$)+H$_2$O is so large.

Figure 4 shows the cuts of the adiabatic PESs for the lowest six electronic states of NO with H$_2$O as a function of the intermolecular distance between NO and H$_2$O, $R_{ON}$, obtained by performing constrained geometry optimizations on D$_2$. We used the nonplanar collision complex with $R_{ON} = 1.91$ Å as the starting point for these adiabatic PESs. The two lowest energy states are labeled as $D_0 (\chi^2\Pi)$ and $D_1 (\chi^2\Pi)$, representing the half-filled $\pi^*$ orbital of the NO doublet radical parallel with or perpendicular to the plane of H$_2$O. These two states show degeneracy at large $R_{ON}$ but have different energies at closer intermolecular distances due to the intermolecular interactions between NO and H$_2$O. At large intermolecular distances, the $D_2 (A^2\Sigma^+)$ state is the 3$s\sigma$ Rydberg state of NO mainly built from the 3$s$ atomic orbitals. $D_3 (C^2\Pi)$ and $D_4 (C^2\Pi)$ are 3$p\pi$ Rydberg states and $D_5 (D^2\Sigma^+)$ is a 3$p\sigma$ Rydberg state; all of these states predominately consist of the unpaired electron residing in the 3$p$ atomic orbitals of NO. The energies are reported relative to the D$_2$ energy at the D$_2$ optimized geometry of NO and H$_2$O constrained at $R_{ON} = 10.0$ Å.
Figure 4. Cuts of the adiabatic PESs of the first six electronic states for NO+H₂O as a function of the distance between the N of NO and the O of H₂O, R_{ON}. All energies are reported relative to the D₂ state at R_{ON} = 10 Å. Note that long-range intermolecular attractions on D₂ lead to a collision complex (shown in the inset) with a relative energy of -0.57 eV. Unlike Figure 2, no low-energy D₂-D₁ conical intersection is present. The SOMOs associated with the D₁ and D₂ states are shown to the right of the PESs; these were evaluated at R_{ON} = 4.01 Å with an isovalue of 0.04.

As shown in Figure 4, the D₂ PES decreases in energy as the two molecules move closer together, signifying increased attractive intermolecular interactions. Eventually, the D₂ PES reaches a minimum at R_{ON} = 1.91 Å, where the energy of D₂ is -0.57 eV, well below the asymptotic limit. At intermolecular distances below 1.91 Å, the D₂ PES increases in energy as R_{ON} decreases, exceeding the asymptotic limit when R_{ON} < 1.55 Å. The D₀ and D₁ PESs are purely repulsive for all the intermolecular distances considered in Figure 4, with D₁ increasing faster as R_{ON} is reduced than D₀. The smallest energy gap between the D₂ and D₁ states identified in Figure 4 is 0.16 eV which occurs at R_{ON} = 1.55 Å and a D₂ relative energy of -0.02 eV. The higher-lying Rydberg
excited states, D$_3$-D$_6$, remain well-separated energetically from D$_2$ at all intermolecular distances that we examined in Figure 4.

The cuts of the NO+H$_2$O PESs shown in Figure 4 exhibit important similarities and differences from those of NO + CO shown in Figure 2. The D$_2$ PESs of both systems exhibit long-range attractions that facilitate electronic quenching. However, the magnitude of these intermolecular attractions is larger for NO (A$^2\Sigma^+$) + H$_2$O than for NO (A$^2\Sigma^+$) + CO. For example, the relative energy at a 3.0 Å intermolecular distance is -0.23 eV for NO (A$^2\Sigma^+$) + H$_2$O but only -0.06 eV for NO (A$^2\Sigma^+$) + CO. Moreover, while a large variety of initial intermolecular orientations of NO (A$^2\Sigma^+$) + H$_2$O are funneled to the same minimum-energy geometry, the PES cuts shown in Figure 2 are representative of a very limited range of initial intermolecular orientations of NO (A$^2\Sigma^+$) + CO; the majority of initial intermolecular orientations of NO (A$^2\Sigma^+$) + CO are not associated with a downhill pathway to a D$_2$-D$_1$ conical intersection. The stronger and less orientationally-dependent intermolecular attractions of NO (A$^2\Sigma^+$) + H$_2$O relative to NO (A$^2\Sigma^+$) + CO helps to explain the much larger electronic quenching cross section of H$_2$O. Figure 2 shows the presence of a D$_2$-D$_1$ conical intersection at an energy well below the asymptotic limit for the NO + CO system. No such low-energy D$_2$-D$_1$ conical intersection is present in Figure 4 for NO + H$_2$O. Since the experimental electronic quenching cross section of NO (A$^2\Sigma^+$) with H$_2$O is 20 times higher than with CO, a low-energy D$_2$-D$_1$ conical intersection must exist for NO + H$_2$O. Therefore, Figure 4 suggests that the pathway to the D$_2$-D$_1$ conical intersection responsible for electronic quenching involves a second nuclear degree of freedom beyond decreasing the intermolecular distance. Finally, we note that while Figure 2 shows an avoided crossing between the D$_2$ and D$_4$ states of NO + CO at $R_{CN} = 2.50$ Å, Figure 4 shows that no such avoided crossing occurs for the NO and H$_2$O system.
Before identifying a feasible pathway to a D₂-D₁ conical intersection, we first applied the analysis shown in Figure 3 to NO (A²Σ⁺) + H₂O to determine if a harpoon mechanism is responsible for the intermolecular attractions on the D₂ PES. Figure 5A shows the total spin densities of the NO and H₂O molecules, acquired by summing the Löwdin atomic spin densities in each molecule, as a function of the intermolecular distance, R_ON. Similarly, Figure 5B shows the total partial charges of the NO and H₂O molecules. In both panels, the NO data is shown in blue while the H₂O data is represented in red. For R_ON ≤ 4.75 Å, the spin densities and partial charges were evaluated at the same geometries as were used in Figure 4. However, for 4.75 Å < R_ON < 10.00 Å, the Löwdin population analysis was performed on geometries obtained by rigidly increasing R_ON from the optimized geometry with R_ON=4.75 Å. No geometry optimizations were performed for these R_ON to bypass the orientational rearrangements that occurred in our constrained geometry optimizations when R_ON > 4.75 Å; such orientational rearrangements led to misleading plots by making R_ON no longer the smallest intermolecular distance. The inflection present in both panels of Figure 5 around R_ON=4.75 Å is a byproduct of this change in the procedure used to generate the molecular geometries.
Figure 5. Löwdin population analysis for the total spin densities (panel A) and partial charges (panel B) of NO and H$_2$O as a function of R$_{ON}$. For R$_{ON}$$\leq$4.75 Å, the geometries are those from Figure 4, while for 4.75$<$R$_{ON}$, the intermolecular distance was rigidly scanned to prevent unwanted changes to the intermolecular orientation. The total spin density and partial charge on each molecule are obtained by combining the values associated with each atom. Similar to Figure 3, this data shows evidence of electron transfer from NO ($A^2\Sigma^+$) to H$_2$O, creating a transient ion pair of NO$^+$ and H$_2$O$^-$ which facilitates increased intermolecular attractions.

Figure 5A shows that, on D$_2$, the spin density is localized on NO at large intermolecular distances. As the molecules move closer together, the spin density becomes delocalized between both molecules. When R$_{ON} < 3.01$ Å, the spin density becomes predominately concentrated onto H$_2$O, which is consistent with electron transfer occurring from the electronically excited NO to the H$_2$O. Figure 3A shows a similar rearrangement of the spin density in the NO ($A^2\Sigma^+$) + CO system, which occurs at a slightly closer intermolecular distance between $R_{CN} = 2.75$ Å and $R_{CN} = 2.50$ Å.

Turning to Figure 5B, we see the expected result of zero partial charge for both NO and H$_2$O at large intermolecular distances. Beginning at approximately $R_{ON} = 3.41$ Å, the partial charges dramatically increase, with the largest magnitude occurring at $R_{ON} = 2.21$ Å with values of +0.601 and -0.601 for NO and H$_2$O, respectively. Collectively, the data presented in both panels of Figure
5 suggests that the attractions between NO \((A^2\Sigma^+)\) and H\(_2\)O are driven by electron transfer from NO to H\(_2\)O, creating a transient ion pair of NO\(^+\) and H\(_2\)O\(^-\) which Coulombically attract one another. As such, a harpoon mechanism is operative for this system as it is for NO \((A^2\Sigma^+) + CO\).

Further support for the D\(_2\) state exhibiting significant charge-transfer character at intermediate intermolecular distances comes from the SOMOs for the D\(_2\) state at representative \(R_{ON}\) displayed in Figure 6. At \(R_{ON} = 3.61\) Å, the electron density amplitude is centered on NO and shows clear 3s\(\sigma\) character. At the minimum energy geometry on D\(_2\) with \(R_{ON} = 1.91\) Å, the electron density shifts onto H\(_2\)O, consistent with electron transfer occurring from NO to H\(_2\)O. Figure 6 further shows that the SOMO at \(R_{ON} = 1.91\) Å resembles the LUMO of H\(_2\)O, which is an antibonding \(\sigma\) orbital for both O-H bonds. At \(R_{ON} = 1.61\) Å, a small amount of electron density is shifted to the 2p\(\pi^*\) molecular orbital state of NO, but the majority remains primarily localized on the H\(_2\)O. This redistribution of electron density from H\(_2\)O and back to NO likely reflects orbital overlap between the two molecules facilitating increased electron delocalization. Figure 5 shows that a consequence of this redistribution of electron density back onto NO is a decrease in the spin density and partial charge on H\(_2\)O at distances below \(R_{ON} = 1.91\) Å.
In addition to the relative energies, we also analyzed the geometric changes in both molecules that occurred as $R_{ON}$ was reduced along the pathway shown in Figure 4. These changes give valuable clues as to which degrees of freedom most effectively facilitate nonradiative relaxation. At both $R_{ON} = 10$ Å and 3.61 Å, the bond length of N-O is 1.06 Å and the O-H bond lengths are both 0.96 Å. The bond angle of H$_2$O slightly decreases from $\theta_{HOH} = 104.4^\circ$ at $R_{ON} = 10$ Å to $\theta_{HOH} = 103.1^\circ$ at $R_{ON} = 3.61$ Å. At the minimum energy geometry on D$_2$, $R_{ON} = 1.91$ Å, the N-O bond length increases to 1.09 Å but the H$_2$O bond angle remains at $\theta_{HOH} = 103.6^\circ$. The largest geometric change involves the elongation of the O-H bonds of H$_2$O, which increase to 1.01 Å and 0.99 Å. This elongation of the O-H bonds of H$_2$O is consistent with a harpoon mechanism as electron density shifts from NO into a $\sigma^*$ molecular orbital of H$_2$O, which destabilizes the O-H bonds. At $R_{ON} = 1.56$ Å, the N-O bond length increases significantly to 1.14 Å, the H$_2$O bond angle increases to $\theta_{HOH} = 111.5^\circ$, and the two O-H bond lengths remain at 1.01 Å and 0.99 Å. The increase in the N-O bond length reflects the presence of electron density in the 2p$\pi^*$ MO of NO shown in Figure 6.
Because Figure 4 does not contain a low-energy D$_2$-D$_1$ conical intersection along $R_{ON}$, at least another nuclear degree of freedom must be involved in facilitating the nonradiative relaxation responsible for the large electronic quenching cross section of NO ($A^2\Sigma^+$)+H$_2$O. We first hypothesized that the O-N-O-H torsion angle ($\phi_{ONOH}$) could be involved and performed a series of relaxed scans of $\phi_{ONOH}$ at fixed intermolecular distances. Figure 7 summarizes the variation in the energy of the D$_2$ state with $\phi_{ONOH}$ for four representative $R_{ON}$ distances. As expected, the electronic energy depends more strongly on $\phi_{ONOH}$ as the intermolecular distance is reduced. Specifically, the D$_2$ energy ranges from -0.51 to -0.55 eV when $R_{ON} = 2.01$ Å and from 0.11 to -0.08 eV when $R_{ON} = 1.56$ Å. Figure 7 further shows that the torsion scans contain two minima and two barriers at each $R_{ON}$. The two minima are associated with rotational conformational isomers (rotamers), differing only in the identity of which O-H bond of water is oriented perpendicular to the NO. Both barriers are associated with $C_{2v}$ geometries, with the larger barrier associated with NO bisecting the two O-H bonds that point towards the N-atom of NO. Overall, Figure 7 shows that distortions along $\phi_{ONOH}$ are associated with minimal energy increases at larger intermolecular distances, but the torsional motions become increasingly hindered as $R_{ON}$ is reduced. In particular, the barriers at $R_{ON} = 1.56$ Å lie above the asymptotic limit.
Figure 7. Cuts of the adiabatic D$_2$ PES for ON+H$_2$O as a function of the torsion angles -165° ≤ ϕ$_{ONO}$ ≤ 180° at $R_{ON}$=2.01 Å (black), $R_{ON}$=1.91 Å (red), $R_{ON}$=1.71 Å (purple), $R_{ON}$=1.61 Å (orange), and $R_{ON}$=1.56 Å (blue). All energies are reported relative to the D$_2$ state at $R_{ON}$ = 10 Å. This analysis demonstrates that torsional motion on D$_2$ becomes increasingly hindered as $R_{ON}$ decreases.

Figures S4-S9 in the Supporting Information show how the D$_2$ and D$_1$ energies vary with ϕ$_{ONO}$ at the $R_{ON}$ values considered in Figure 7. At larger $R_{ON}$, varying ϕ$_{ONO}$ does not appreciably reduce $E_{D_2} - E_{D_1}$. For example, at $R_{ON}$=1.91 Å, $E_{D_2} - E_{D_1}$ ranges from 2.59 eV to 2.64 eV. The D$_2$-D$_1$ energy gap is more strongly affected by ϕ$_{ONO}$ at smaller $R_{ON}$. However, the smallest observed value of $E_{D_2} - E_{D_1}$, 0.13 eV at $R_{ON}$=1.56 Å and ϕ$_{ONO}$ = 0°, is only slightly smaller than
the minimal $D_2$-$D_1$ energy gap present in Figure 4, 0.16 eV. As such, we conclude that $\phi_{ONOH}$ is not relevant for the NO ($A^2\Sigma^+$) + H$_2$O electronic quenching pathway.

As mentioned above, the N-O bond length varies significantly along the path shown in Figure 4. Therefore, we explored the extent to which distortions of the N-O bond length modulate $E_{D_2} - E_{D_1}$, the analysis of which is presented in Figure 8 along with Figures S10-S11 in the Supporting Information. As shown in panel A of Figure 8, decreasing the N-O bond length somewhat reduces the $D_2$-$D_1$ energy gap when $R_{ON}$=1.91 Å. However, $E_{D_2} - E_{D_1}$ exceeds 1.8 eV for all N-O bond lengths for which $E_{D_2} < 0$. Panel B shows that when the intermolecular distance is reduced to $R_{ON}$=1.61 Å, $E_{D_2} - E_{D_1}$ depends much more strongly on the N-O bond length. Indeed, decreasing the N-O bond length from 1.12 Å to 1.05 Å causes $E_{D_2} - E_{D_1}$ to decrease from 0.42 eV to 0.07 eV. Similar to Figure 4, this pathway to a $D_2$-$D_1$ conical intersection is associated with a significant increase in energy, with $E_{D_2}$ becoming greater than the asymptotic limit. As a result, while the N-O bond length changes appreciably along the path shown in Figure 4, distorting it...
away from its equilibrium value at the D$_2$ collision complex does not provide an effective means for the nonradiative relaxation of NO ($A^2\Sigma^+$) + H$_2$O.

The other geometric parameters that undergo significant changes along the path shown in Figure 4 are the O-H bond lengths of water. As such, in Figure 9, we consider how the energy of the D$_2$ state varies as the O-H bond lengths of water are stretched at a series of intermolecular distances. In panel A, we focus on a relaxed scan along $r_{\text{OH}_A}$, the O-H bond that is oriented perpendicular to NO, at four different fixed $R_{\text{ON}}$. Panel B presents the same data for the other O-H bond length, $r_{\text{OH}_B}$. To maintain a parallel orientation between NO and the stretched O-H bond, the relaxed $r_{\text{OH}_B}$ scans shown in panel B were performed at a fixed torsion angle of $\phi_{\text{ONO}_B} = -179.9^\circ$ in addition to a fixed $R_{\text{ON}}$. Without this torsion angle constraint, the geometry optimization resulted in $r_{\text{OH}_B}$ becoming oriented perpendicular to NO, thus swapping positions with $r_{\text{OH}_A}$.
Figure 9. Cuts of the adiabatic D$_2$ PES of ON+H$_2$O as a function of the O-H bond length $r_{OH_A}$ (panel A) or $r_{OH_B}$ (panel B) at a fixed intermolecular distance of $R_{ON} = 1.91$ Å (dark red), $R_{ON} = 1.81$ Å (red), $R_{ON} = 1.787$ Å (dark blue), and $R_{ON} = 1.76$ Å (blue). All energies are reported relative to the D$_2$ state at $R_{ON} = 10$ Å. The O-H bond lengths $r_{OH_A}$ and $r_{OH_B}$ are defined in the insets. Note that increasing $r_{OH_A}$ is associated with a modest increase in energy, ranging from 0.32 eV at $R_{ON} = 1.91$ Å to 0.15 eV at $R_{ON} = 1.76$ Å. Increasing $r_{OH_B}$ is associated with a larger increase in $E_{D_2}$.

Focusing first on the $E_{D_2}$ versus $r_{OH_A}$ data shown in Figure 9A, stretching this O-H bond causes the energy of the D$_2$ state to modestly increase. The most dramatic change occurs at $R_{ON}=1.91$ Å, where increasing $r_{OH_A}$ causes $E_{D_2}$ to increase from -0.57 eV to -0.25 eV. Importantly, all of these data points lie well below the D$_2$ ($A^2\Sigma^+$) asymptotic limit, suggesting that these distortions are kinetically viable for the collision complex even at low temperatures. At smaller intermolecular distances, the relative energy initially increases as $r_{OH_A}$ is stretched but eventually turns over and begins to decrease, suggesting the existence of another local minimum on the D$_2$ PES consistent with a significantly stretched or even broken O-H bond. The largest value of $E_{D_2}$ observed in the relaxed scans at $R_{ON} = 1.81$ Å, 1.787 Å, and 1.76 Å is -0.39 eV, -0.41 eV, and
-0.42 eV, respectively. Moreover, at the elongated O-H bond lengths with \( r_{OH_A} > 1.1 \text{ Å} \), decreasing \( R_{ON} \) is associated with lower energies on \( D_2 \). As such, stretching this O-H bond drives the two molecules closer together.

The data presented in panel B of Figure 9 displays similar trends as those shown in panel A. Increasing \( r_{OH_B} \), however, has a significantly larger impact on \( E_{D_2} \) than increasing \( r_{OH_A} \). Specifically, at \( R_{ON} = 1.91 \text{ Å} \), the energy of the D\(_2\) state ranges from -0.57 eV to -0.06 eV, which is over twice the range shown in panel A. Similarly, the barriers in the relaxed \( r_{OH_B} \) scans at \( R_{ON} = 1.81 \text{ Å}, 1.787 \text{ Å}, \) and 1.76 \text{ Å} occur at -0.22 eV, -0.24 eV, and -0.27 eV, respectively. Because distortions along \( r_{OH_B} \) result in a 1.5-2 times greater increase in energy on \( D_2 \) than distortions along \( r_{OH_A} \), the \( r_{OH_A} \) coordinate is likely more relevant to the photochemistry of NO (A\(^2\Sigma^+\)) + H\(_2\)O.

Figure 10 shows the \( D_2 \) and \( D_1 \) energies as a function of \( r_{OH_A} \) at a fixed intermolecular distance of \( R_{ON} = 1.787 \text{ Å} \). The energy of the \( D_1 \) state increases rapidly as \( r_{OH_A} \) increases while \( E_{D_2} \) displays a much weaker dependence on \( r_{OH_A} \). Indeed, the \( D_2 \) PES appears relatively flat at the scale of this plot. Importantly, the \( D_2-D_1 \) energy gap is observed to decrease as \( r_{OH_A} \) increases, reaching a minimum value of 0.06 eV at \( r_{OH_A} = 1.365 \text{ Å} \). Attempts to obtain optimized geometries at slightly larger values of \( r_{OH_A} \) were unsuccessful due to the near-degeneracy of the \( D_2 \) and \( D_1 \) states. Nevertheless, it is clear from Figure 10 that a \( D_2-D_1 \) conical intersection will occur at a geometry with \( R_{ON} = 1.787 \text{ Å} \) and \( r_{OH_A} \) slightly larger than 1.365 \text{ Å}. Moreover, this \( D_2-D_1 \) conical intersection will form at a \( E_{D_2} \approx -0.43 \text{ eV} \), which lies well below the asymptotic limit and only 0.14 eV above the \( D_2 \) minimum energy geometry. As such, once the NO (A\(^2\Sigma^+)\) + H\(_2\)O collision complex is generated, it can readily undergo the distortions necessary to reach this \( D_2-D_1 \) conical intersection.
Figure 10. Cuts of the adiabatic PESs of the D₁ and D₂ states for NO+H₂O as a function of \( r_{OH_A} \) at a fixed \( R_{ON} = 1.787 \, \text{Å} \). All energies are reported relative to D₂ at \( R_{ON} = 10 \, \text{Å} \). The inset cartoons illustrate how these PESs support both reactive electronic quenching, which produces the products HONO+H shown at the right, and nonreactive electronic quenching, which produces NO (\( X^2\Pi \)) and H₂O with the excess energy stored in their nuclear degrees of freedom.

Figures S12-S14 extend the analysis presented in Figure 10 to the intermolecular distances \( R_{ON}=1.91 \, \text{Å}, R_{ON}=1.81 \, \text{Å}, \) and \( R_{ON}=1.76 \, \text{Å} \). For all intermolecular distances, the D₂-D₁ energy gap decreases as \( r_{OH_A} \) increases. Moreover, the initial D₂-D₁ energy gap at \( r_{OH_A}=1.0 \, \text{Å} \) depends sensitively on the intermolecular distance, with \( E_{D_2} - E_{D_1} \) increasing as \( R_{ON} \) increases. For example, at \( r_{OH_A}=1.325 \, \text{Å} \), \( E_{D_2} - E_{D_1} \) is 0.09 eV when \( R_{ON}=1.76 \, \text{Å} \) but 1.30 eV when \( R_{ON}=1.91 \, \text{Å} \). As such, this low-energy pathway to a D₂-D₁ conical intersection involves both decreasing the intermolecular distance and stretching the O-H bond that is approximately perpendicular to the
NO.

As suggested by the insets in Figure 10, the D₂-D₁ conical intersection that is accessible through a combination of decreasing \( R_{ON} \) and increasing \( r_{OH_A} \) provides a pathway for both reactive and nonreactive electronic quenching. In the case of the nonreactive electronic quenching channel (blue arrow), the dramatic stretching of the O-H bond shown in Figure 10 will likely cause the \( \text{H}_2\text{O} \) molecule to gain significant vibrational excitation in a local O-H stretching mode. Therefore, we predict that future VMI experiments on \( \text{NO} (A^2\Sigma^+)+\text{H}_2\text{O} \) nonreactive electronic quenching will observe a vibrational progression in the antisymmetric O-H stretching mode of \( \text{H}_2\text{O} \) with \( \text{NO} (X^2\Pi, \nu'', J'') \) products.

Turning to reactive quenching, the pathway shown in Figure 10 will result in cleavage of an O-H bond of \( \text{H}_2\text{O} \), producing a free H-atom as previously observed in experiments by Umemoto and co-workers.²⁵ As discussed above, there is an energetic driving force on D₂ for decreasing \( R_{ON} \) at elongated \( r_{OH_A} \). This supports the formation of HONO as the co-product in the reactive electronic quenching pathway. Note that the reactive pathway will involve a non-adiabatic transition from D₂ to D₁ as the D₁ state has previously been shown to adiabatically correlate to \( \text{H} (2\text{S})+\text{HONO} (X^1\text{A}^\prime) \).

To further demonstrate the plausibility of reactive quenching, we calculated the electronic energies of \( \text{cis}-\text{HONO}+\text{H} \) and \( \text{trans}-\text{HONO}+\text{H} \) with and without zero-point energy (ZPE) corrections; this data is summarized in Table 2.⁴⁵-⁴⁷ The relative energies of \( \text{cis}-\text{HONO}+\text{H} \) and \( \text{trans}-\text{HONO}+\text{H} \) were found to be -2.07 eV and -2.09 eV (-2.25 eV and -2.27 eV with ZPE corrections), respectively. These energies are both well below the asymptotic limit and hence indicate that HONO+H formation is thermodynamically favorable relative to \( \text{NO} (A^2\Sigma^+) + \text{H}_2\text{O} \).
The energy released by this reaction will partition into the translational kinetic energies of the co-products along with the rotational and vibrational degrees of freedom of HONO. In particular, Umemoto and co-workers used the Doppler profiles of the H-atoms produced from the reactive electronic quenching process to determine an average translation kinetic energy of 1.17 eV.\textsuperscript{25}

Table 2. Relative energies of predicted product outcomes from reactive electronic quenching with and without ZPE corrections.

<table>
<thead>
<tr>
<th>Products</th>
<th>Relative Electronic Energy (eV)\textsuperscript{a}</th>
<th>Relative Electronic Energy + ZPE (eV)\textsuperscript{a,b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-HONO + H (1s)</td>
<td>-2.07</td>
<td>-2.25</td>
</tr>
<tr>
<td>trans-HONO + H (1s)</td>
<td>-2.09</td>
<td>-2.27</td>
</tr>
<tr>
<td>NO (X) + OH (X) + H (1s)</td>
<td>0.19</td>
<td>-0.17</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Energies of possible products relative to the D\textsubscript{2} asymptotic limit.

\textsuperscript{b}ZPE corrections based on experimentally determined vibrational constants.\textsuperscript{45–47}

Analysis of the pathway shown in Figure 10 allows us to make predictions about the properties of the HONO produced in the reactive electronic quenching pathway. As suggested by the geometries shown in Figure 10, the reactive quenching pathway will preferentially form trans-HONO because the D\textsubscript{2} PES steers NO+H\textsubscript{2}O into geometries where |ϕ\textsubscript{ONO H}| = 180 °. Because the ON-OH bond is formed in the reactive electronic quenching, the trans-HONO will likely have significant internal energy in the ON-OH stretch local mode. Similarly, because the N-O bond length of the NO moiety elongates along the reactive quenching pathway, the local vibrational stretching mode associated with this coordinate may also contain internal energy. It is unlikely that the trans-HONO will be generated with sufficient energy in its torsional mode to surmount the 0.515 eV barrier to cis-HONO. However, it is possible that this isomerization could occur through a combination of tunneling and intramolecular vibrational energy redistribution.\textsuperscript{48} Finally, we considered the feasibility of the trans-HONO undergoing decomposition to generate NO and OH.
The NO+OH+H channel is marginally viable energetically, with a -0.17 eV relative energy with ZPE. However, the limited exothermicity of NO+OH+H formation and the large translational kinetic energies observed in previous experiments suggests that HONO+H will be the major product channel.

In Figures S15-S18, we analyze the D$_2$ and D$_1$ PESs as a function of $r_{\text{OH}_B}$ at different fixed intermolecular distances. Similar to Figure 10, the D$_1$ state rapidly increases in energy as this O-H bond is stretched while the dependence of $E_{D_2}$ is much more modest. As such, increasing $r_{\text{OH}_B}$ causes the D$_2$-D$_1$ energy gap to shrink. However, this occurs at a much lower rate than what is observed in Figure 10 and Figures S12-S14. For example, when $R_{\text{ON}}=1.787$ Å and $r_{\text{OH}_B}=1.365$ Å the D$_2$-D$_1$ energy gap is 0.31 eV. In contrast, when $R_{\text{ON}}=1.787$ Å and $r_{\text{OH}_A}=1.365$ Å the D$_2$-D$_1$ energy gap is a much smaller 0.06 eV. Moreover, as shown in Figure 9 and discussed above, increasing $r_{\text{OH}_B}$ causes a significantly greater increase in the energy of the D$_2$ state than increasing $r_{\text{OH}_A}$. As a result, the dominant electronic quenching pathway likely involves distortions along $r_{\text{OH}_A}$ and $R_{\text{ON}}$, with the $r_{\text{OH}_B}$ coordinate playing a minor role in the dynamics.

**Conclusions**

The PES cuts developed in this study provide clear insights into the photochemical mechanisms responsible for the reactive and nonreactive electronic quenching mechanisms of NO ($A^2\Sigma^+$) with H$_2$O. Long-range intermolecular attractions funnel a wide variety of initial intermolecular orientations of NO ($A^2\Sigma^+$) and H$_2$O to the same minimum-energy geometry at an intermolecular distance of 1.91 Å. These long-range attractive interactions were much stronger and more isotropic than those of NO ($A^2\Sigma^+$) + CO, consistent with the much greater electronic quenching cross section of NO ($A^2\Sigma^+$) + H$_2$O. The attractive intermolecular interactions were
shown to be driven by electron transfer from NO ($A^2\Sigma^+$) to $H_2O$ to create a transient ion pair. This harpoon mechanism was also implicated as the source of the intermolecular attractions in the NO ($A^2\Sigma^+$) + $N_2$ and NO ($A^2\Sigma^+$) + CO systems. From the $D_2$ minimum-energy geometry, distortions involving decreasing the intermolecular distance, $R_{ON}$, and increasing one of the $O-H$ bond lengths, $r_{OH_{A'}}$, reduce the $D_2-D_1$ energy gap and ultimately lead to a $D_2-D_1$ conical intersection. This pathway lies well below the asymptotic limit and is associated with only a very modest energy increase relative to the minimum-energy collision complex on $D_2$. Moreover, this pathway accounts for both reactive and nonreactive electronic quenching.

The analysis presented in this study allows us to make clear predictions for future experimental studies on this system. The nonreactive electronic quenching pathway will tend to produce $H_2O$ which is vibrationally excited in its antisymmetric $O-H$ stretching mode because the pathway to the $D_2-D_1$ conical intersection involves a significant stretching of one of the $O-H$ bonds. As such, future VMI studies will likely observe a vibrational progression in the antisymmetric $O-H$ stretching mode when NO ($\chi^2\Sigma_g$) is formed. Reactive electronic quenching will form $H$ atoms and trans-HONO with internal energy primarily localized in the ON-OH and N-O stretching modes. The branching between the nonreactive and reactive electronic quenching pathways is one major observable that we are unable to address in this study; this will be the subject of a future study employing non-adiabatic dynamics simulations.

HONO is a major source of OH radicals during the daytime.$^{49-52}$ A key radical intermediate in the atmosphere and combustion, OH radicals are arguably the most important oxidizers in these environments since they initiate the removal of gaseous pollutants.$^{53,54}$ With the lowest energy transition $A^1A''-X^1A'$ of HONO occurring between 300 – 400 nm, this critical reservoir readily undergoes solar photolysis during the dawn and daytime hours to yield greater than 50% of the
atmospheric OH radical concentration in major cities.\textsuperscript{55} In urban areas with large concentrations of NO\textsubscript{x} compounds, which includes NO, in addition to atmospheric H\textsubscript{2}O, it is likely that quenching of NO (A\textsuperscript{2}\Sigma\textsuperscript{+}) with H\textsubscript{2}O at higher altitudes is a source of daytime HONO, which will readily decompose as a sink to OH + NO radicals. Therefore, this catalytic cycle of NO may serve as an important source of OH radicals, enriching the local atmospheric chemistry in polluted areas.

**Conflicts of Interest**

There are no conflicts of interest to declare.

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