

Relaxation of the molecular nitric oxide ultracold plasma to a state of constant high- n , high- ℓ Rydberg density

August 12, 2020

1 Coarse-grained kinetic mechanism for avalanche to plasma and quench

For future reference, let us define concentrations of the following key species in the nitric oxide ultracold plasma:

$$A = [\text{NO}^{**}] \quad (1)$$

which represents the density of NO molecules in high- n , high- ℓ Rydberg states. This population includes bound states of multiple NO^+ charge centres, screened to a net charge of +1.

$$D = [\text{NO}^+] \text{ or } [\text{e}^-] \quad (2)$$

defined always equal by quasi-neutrality.

$$R = [\text{NO}^*] \text{ or } [\text{N}(^4\text{S}) + \text{O}(^3\text{P})] \quad (3)$$

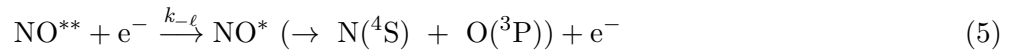
where NO^* represents low- ℓ Rydberg states of any n . In this coarse-grained approach, we assume that these predissociate to neutral atoms on a timescale faster than ℓ -mixing.

We represent a coarse-grained mechanism for evolution following initial avalanche by the following reactions:

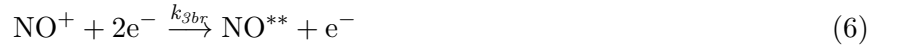
Electron impact ionization



ℓ -mixing



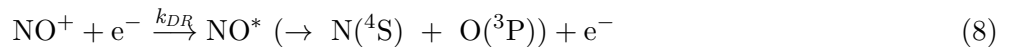
Three-body recombination



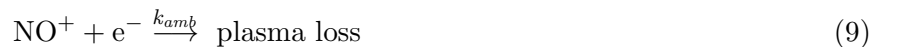
Hydrodynamic recombination (CT bifurcation accompanied by electron quench)



Dissociative recombination (indirect or direct DR)



Loss of NO^+ ions to ambipolar expansion



2 Coupled rate equations for the time evolution of $[\text{NO}^{**}]$ and $[\text{NO}^+]$

This mechanism gives rise to the following coupled rate equations:

Evolution of long-lived NO^{**}

$$\frac{d[\text{NO}^{**}]}{dt} = -k_I[\text{NO}^{**}][e^-] - k_{-\ell}[\text{NO}^{**}][e^-] + k_{3br}[\text{NO}^+][e^-]^2 + k_{CT}[\text{NO}^+][\text{NO}^{**}][e^-] \quad (10)$$

Incorporation of NO^+ ions.

$$\frac{d[\text{NO}^+]}{dt} = -k_{amb}[\text{NO}^+] + k_I[\text{NO}^{**}][e^-] - k_{3br}[\text{NO}^+][e^-]^2 - k_{CT}[\text{NO}^+][\text{NO}^{**}][e^-] - k_{DR}[\text{NO}^+][e^-] \quad (11)$$

Here, we implicitly assume that NO^* appears only as a possible intermediate in 1) the predissociation of NO^{**} induced by ℓ -mixing, and 2) the indirect dissociative recombination of $\text{NO}^+ + e^-$. The short lifetime of NO^* implies little effect of k_ℓ after the avalanche.

As a practical matter, quasi-neutrality assures that $[\text{NO}^+] = [e^-]$. We can refer to our coupled rate-equation codes to determine realistic initial densities immediately after avalanche and effective average values for these rate constants. Here, for the purpose of example, we make some reasonable assumptions.

In general, I think that we can assume that,

$$k_{CT} \gg k_\ell > k_I \gg k_{-\ell} \quad (12)$$

and

$$k_I > k_{DR} \quad (13)$$

During the time interval from 5 to 500 μs , the plasma forms a Saha-like quasi equilibrium in which.

$$k_I \approx k_{3br}[e^-] \quad (14)$$

Again, we will refer to our coupled rate-equation codes to verify these assumptions.

In a notation of A and D , we can write Eq (10)

$$\dot{A} = -k_I AD - k_{-\ell} AD + k_{CT} AD^2 + k_{3br} D^3 \quad (15)$$

$$= -(k_I + k_{-\ell}) AD + k_{CT} AD^2 + k_{3br} D^3 \quad (16)$$

Or, in compact form:

$$\dot{A} = -k^{**} AD + k_{CT} AD^2 + k_{3br} D^3 \quad (17)$$

and Eq (11)

$$\dot{D} = k_{amb} D + k_I AD - k_{CT} AD^2 - k_{DR} D^2 - k_{3br} D^3 \quad (18)$$

3 Demonstrated evolution of a coarse-grain system of coupled rate equations to define a single critical density of NO^{**} for a range of initial Rydberg gas densities

The prompt Penning ionization of Rydberg molecule pairs that populate the leading edge of the nearest neighbour distribution forms an initial population of electrons. These electrons trigger an avalanche of electron-impact ionization processes, accompanied by ℓ -mixing that causes the plasma to evolve to a distribution of high- n , high- ℓ Rydberg molecules, NO^+ ions and electrons that form the initial populations A_0 (NO^{**}) and D_0 (NO^+) that figure in the coarse-grained kinetics above.

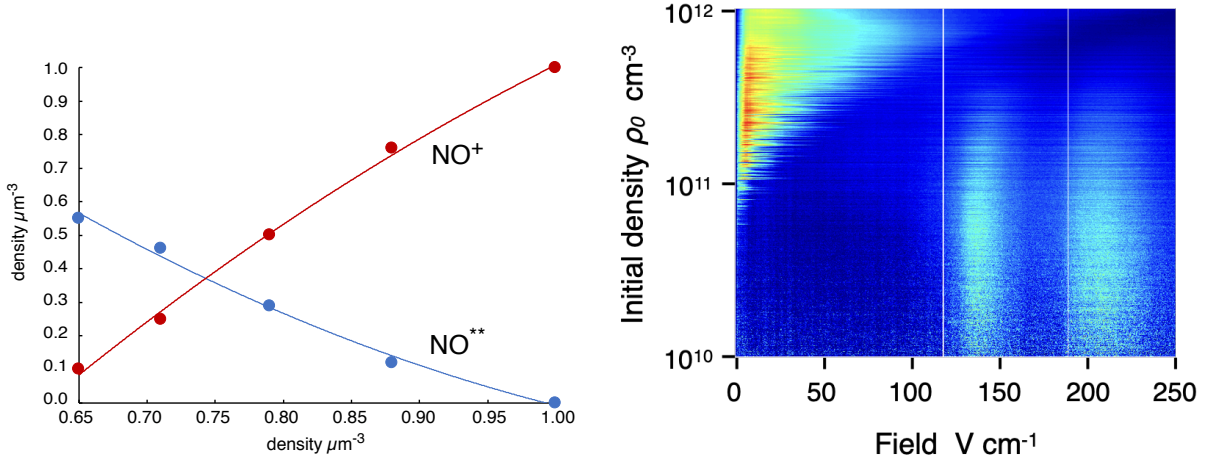


Figure 1: (left) Assumed partial densities of high- n , high- ℓ Rydberg molecules, NO^{**} and NO^+ ions hypothetically produced by electron-impact avalanche, as listed in Table 1, and plotted here as a function of total initial Rydberg gas density. (right) Experimental measure of electron binding energy to NO^+ as n_0 Rydberg molecules, as high- n Rydberg molecules and as a space charge of NO^+ ions.

The initial peak density, ρ_0 , together with the initial principal quantum number, n_0 , determine the initial densities of NO^{**} and NO^+ for the purposes of solving coarse-grained coupled differential equations. Figure 1 shows a representative possible set of NO^{**} and NO^+ densities after avalanche and ℓ -mixing, before expansion, charge transfer and quench.

Table 1: Assumed initial high-Rydberg and ion densities and a set of effective rate constants governing a coarse-grained mechanism for the relaxation of the nitric oxide Rydberg gas to a critical state

| A_0 μm^{-3} | D_0 μm^{-3} | k_{amb} μs^{-1} | k_I $\mu\text{m}^3\mu\text{s}^{-1}$ | $k_{-\ell}$ $\mu\text{m}^3\mu\text{s}^{-1}$ | k_{CT} $\mu\text{m}^6\mu\text{s}^{-1}$ | k_{3br} $\mu\text{m}^6\mu\text{s}^{-1}$ | k_{DR} $\mu\text{m}^3\mu\text{s}^{-1}$ | k_ℓ $\mu\text{m}^3\mu\text{s}^{-1}$ |
|-----------------------------|-----------------------------|---------------------------------|--|--|---|--|---|---|
| 0.00 | 1.00 | 2 | 2 | 0.1 | 50 | 2 | 2 | 3 |
| 0.12 | 0.75 | 2 | 2 | 0.1 | 50 | 2 | 2 | 3 |
| 0.29 | 0.50 | 2 | 2 | 0.1 | 50 | 2 | 2 | 3 |
| 0.46 | 0.25 | 2 | 2 | 0.1 | 50 | 2 | 2 | 3 |
| 0.55 | 0.10 | 2 | 2 | 0.1 | 50 | 2 | 2 | 3 |

Table 1 collects these representative initial densities together with reasonable estimates of rate constants, k_{amb} and k_{CT} , chosen to phenomenologically describe the gross processes of ion loss owing to ambipolar expansion, as well as three-body, $\text{NO}^+ + e^- + \text{NO}^{**}$ quench and recombination. This table also includes average rate constants for elementary electron-electron-ion reactions representative of the state-detailed processes that govern the evolution to a plasma quasi equilibrium.

For this particular coarse-grain representation, any pair of post-avalanche representative densities of NO^+ and NO^{**} evolves to form to the same long-time density of NO^{**} , as shown in Figure 2. This begs the question, what can we expect find by the numerical integration of a full, state-detailed, set of coupled rate equations evolving in the density gradient of an ellipsoidal shell system.

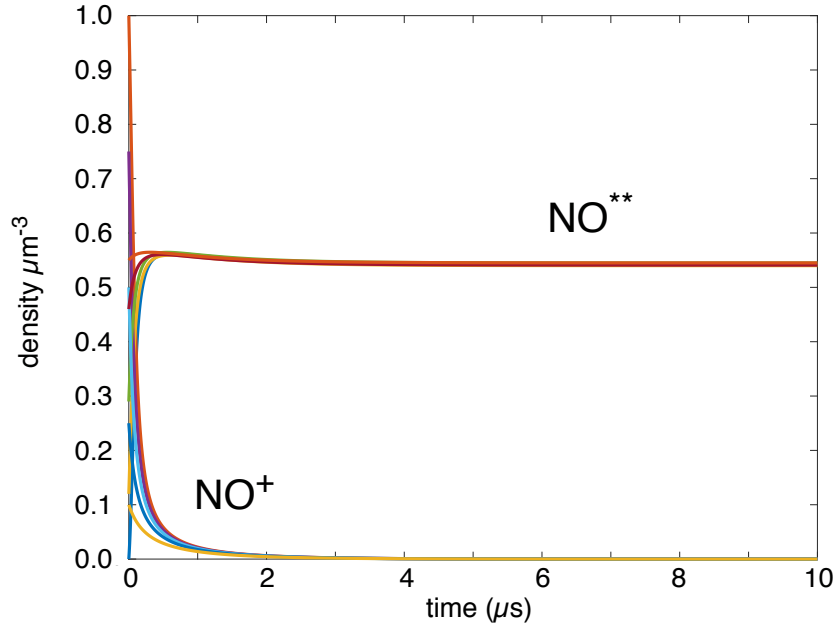


Figure 2: Evolving average densities of high- n , high- ℓ Rydberg molecules, NO^{**} and NO^+ ions predicted by a coarse-grained model for the coupled kinetics of ambipolar expansion, electron impact ionization, three-body recombination, ℓ -mixing, dissociative recombination and hydrodynamic recombination (resonant electron transfer and bifurcation accompanied by electron quench in the nitric oxide ultracold plasma, using the rate parameters listed in Table 1 for five different initial densities of NO^+ ions and high-Rydberg molecules produced in the electron-impact avalanche of a hypothetical Rydberg gas.

4 A search for self-organized criticality in full set of coupled rate equations

Let us incorporate the effects of ion loss and charge-transfer assisted three-body recombination by applying a simple ansatz in treating the kinetics of evolution in each shell.

1. Let us allow every shell to lose NO^+ ions and electrons at a rate, $d[\text{NO}^+]/dt = k_{amb}[\text{NO}^+]$. We may wish to allow k_{amb} to decrease linearly with electron temperature.
2. Let us add a term to the coupled rate equations for each Rydberg of quantum number n in each shell, of the form $d[\text{NO}^{**}]/dt = k_{CT}[\text{NO}^{**}][\text{NO}^+][e^-]$, where $[\text{NO}^{**}]$ refers to the density of the Rydberg molecule of quantum number n .
3. As the electron density falls, let us reduce the master predissociation rate constant to zero.