Comprehensive Validation of Electronic Excitation and Ionization Kinetics in Oxygen–Nitrogen–Argon Plasmas

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Background

Recent years have seen a concerted effort to improve models of plasma formation in hypersonic flows[1]. Validating these models has long been hampered by a lack of experimental data capable of characterizing ionization and its precursor processes – electronic excitation in particular. Meeting this need requires shock tube experiments that probe the relevant species in suitable test gas mixtures with low detection limits, low measurement uncertainty, and high time resolution.

In previous works, the authors carried out experimental and modeling studies of electronic excitation and ionization in 1–2% N_2–Ar[2,3] and 1% O_2–Ar[4,5] mixtures. Measurements of atomic excited state number densities, together with electron number density in the O_2–Ar case[6], validated collisional-radiative models of these mixtures at a precision not previously achievable. A key limitation, however, was the narrow range of mixtures these studies could access: typically 98–99% argon, a dilution needed to sustain the high temperatures required for detectable populations of the target electronic levels.

Two recent advances lift this constraint. The development of a ring amplified shock tube in the Hanson Research Group at Stanford University has increased the sensitivity of infrared laser absorption diagnostics by up to a hundredfold[7], opening a new generation of experiments at lower temperatures, where the heavy-particle excitation processes of greatest interest dominate, and in less dilute, more diverse mixtures[8]. Alongside this gain, a suite of new diagnostics has come online, covering electronically excited states of O, N, Ar, N_2, and NO, as well as free electrons and the ground electronic level of N_2^+.

In this work, we present a detailed modeling study of data from a recent Stanford shock tube campaign spanning pure argon, O_2–Ar, N_2–Ar, and O_2–N_2–Ar mixtures at varying concentrations, with mixtures chosen to isolate key rate coefficients of interest to hypersonic flow modeling. In some of these experiments, time histories of as many as twelve parameters were measured simultaneously, offering an unprecedented opportunity to constrain and improve models of electronic excitation and ionization in shock-heated gases.

Methodology

Across the experimental campaign, number densities were measured for free electrons, $N_2^+(X^2\Sigma_g^+)$, $N_2(A^3\Sigma_u^+)$, $NO(A^2\Sigma^+)$, the fourth through seventh electronic levels of atomic oxygen, the fourth, fifth, and eighth levels of

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[2]Finch et al.(2023), DOI: 10.1021/acs.jpca.2c07839.
[3]T.T. Aiken and Boyd(2024), DOI: 10.1063/5.0179577.
[4]Li, Y. Wang, et al.(2021), DOI: 10.1103/PhysRevE.103.063211.
[5]T.T. Aiken and Boyd(2024), DOI: 10.1103/PhysRevE.109.045203.
[6]Li, S. Wang, et al.(2021), DOI: 10.1088/1361-6595/abdd12.
[7]Strand et al.(2025), DOI: 10.1364/OE.571994.
[8]Merrell et al.(2026), DOI: 10.2514/6.2025-1995.

atomic nitrogen, and the second and twelfth electronic levels of argon. Doppler broadening of several atomic lines yields the translational temperature, while Stark effects allow the free electron temperature and number density to be probed. The mixtures span pure argon, 1–30% N_2 in Ar, 1–15% O_2 in Ar, and several N_2–O_2 mixtures dilute in argon.

The experiments are simulated with the TERRA code at the University of Colorado Boulder using a recently developed three-temperature collisional-radiative (CR) model[9]. Each simulation includes an enthalpy source term accounting for the non-ideal pressure rise measured in the experiment, following prior findings on the importance of such a term[10].

For each experiment, a sensitivity analysis is performed with more than 1,000 uncertain parameters, each with literature-informed uncertainty intervals[11]. Sobol' indices and mutual information are computed at each data point; the latter incorporates the measurement uncertainty to quantify how much each measurement can reduce the uncertainty in a given rate parameter. Together, these analyses identify which parameters are active in shaping the measured time histories across all experiments and diagnostics, and reveal whether each measurement falls within the model's range of feasible predictions. A measurement that does not signals a clear need for model improvement, potentially through the inclusion of collisional processes not previously accounted for.

With the active parameter set established, the final step is a Bayesian inference of the most sensitive rate parameters using the same surrogates built for the sensitivity analysis. Here we focus on a limited set of experiments, with the goal of developing an inference framework that scales to the full dataset. The simplest mixture to probe is pure argon, followed by O_2–Ar and N_2–Ar, likely leveraging data from the literature or from previous test campaigns to constrain additional rates in the model, such as those for dissociation.

Results

Comparisons with the measured time histories are underway for the argon, O_2–Ar, N_2–Ar, and O_2–N_2–Ar data. In the O_2–N_2–Ar and O_2–Ar mixtures, predicted oxygen, argon, and nitrogen excited state number densities overshoot the measurements by up to a factor of three across much of the dataset. Predictions of N_2(A) and NO(A), by contrast, agree well with the measurements, except at very early times where the models overpredict the transient peak in these states.

Electron number density predictions in N_2–O_2–Ar likewise exceed the measurements, with charge exchange involving N_2^+ playing a major role in the overall ionization rate. The new N_2^+ measurements offer direct insight on this process, allowing models of charge exchange to be substantially improved and the electron number density data to be leveraged further for validating ionization reactions in hypersonic air flows.

Conclusion

The data recently gathered at Stanford offer an unprecedented opportunity to advance the state of the art in kinetic models of excitation and ionization behind strong shock waves. Through detailed comparison, sensitivity analysis, and Bayesian inference, we aim to exploit this extensive dataset to reduce the uncertainty in existing kinetic models for ionized hypersonic flows.

[9] T.T. Aiken, Boyd, and Adamovich(2025), DOI: 10.1063/5.0294530.
[10] T.T. Aiken and Boyd(2024), DOI: 10.1063/5.0179577.
[11] T.T Aiken et al.(2025), DOI: 10.2514/6.2025-0212.