

Rovibrational state-to-state modeling of nitrogen recombination

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Summary

During the fast cooling of nitrogen flow, N atoms recombine preferentially into high vibrational levels of N₂. Rovibrational levels may not have time to equilibrate into a Boltzmann distribution. In this case, state-to-state kinetic models are necessary to predict the evolution of densities of each internal level. Reliable kinetic models require the knowledge of the rate constants of reactions between internal states. Numerous works have been devoted to this task in the past: empirical, semi-empirical or ab-initio methods have been developed to estimate the rate constants for rotational/vibrational relaxation (2-temperature model [1], SSH theory [2], forced harmonic oscillator theory [3], semi-classical method [4], quasi-classical trajectory method [5]) and dissociation ([5]–[7]).

They have been extensively used and compared for compression flows [8]–[10], where vibrational non-equilibrium occurs because of fast heating.

In this work, we will extend the comparison to fast cooling flows. An analysis of the vibrational distribution function (VDF) and of the main reaction pathways will be performed for each model. Then reduced order models will be proposed to track specifically the evolution of the VDF at a reduced computational cost. The assumption of rotational equilibrium within each vibrational level will be assessed thanks to a rovibrational state specific collisional model [5].

References

- [1] C. Park, *Nonequilibrium Hypersonic Aerothermodynamics*. 1989.
- [2] R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, “Calculation of vibrational relaxation times in gases,” *J. Chem. Phys.*, vol. 20, no. 10, pp. 1591–1599, 1952.
- [3] I. V. Adamovich, S. O. Macheret, J. W. Rich, and C. E. Treanor, “Vibrational Relaxation and Dissociation behind Shock Waves Part 1: Kinetic Rate Models,” *AIAA J.*, vol. 33, no. 6, pp. 1064–1069, 1995.
- [4] G. D. Billing and E. R. Fisher, “VV and VT rate coefficients in N₂ by a quantum-classical model,” *Chem. Phys.*, vol. 43, no. 3, pp. 395–401, Nov. 1979.
- [5] R. Jaffe, D. Schwenke, G. Chaban, and W. Huo, “Vibrational and Rotational Excitation and Relaxation of Nitrogen from Accurate Theoretical Calculations,” in *46th AIAA Aerospace Sciences Meeting and Exhibit*, 2008, no. January, pp. 1–14.
- [6] S. O. Macheret and J. W. Rich, “Nonequilibrium dissociation rates behind strong shock waves: classical model,” *Chem. Phys.*, vol. 174, no. 1, pp. 25–43, Jul. 1993.
- [7] S. O. Macheret and I. V. Adamovich, “Semiclassical modeling of state-specific dissociation rates in diatomic gases,” *J. Chem. Phys.*, vol. 113, no. 17, pp. 7351–7361, 2000.
- [8] C. E. Treanor, J. W. Rich, and R. G. Rehm, “Vibrational Relaxation of Anharmonic Oscillators with Exchange-Dominated Collisions,” *J. Chem. Phys.*, vol. 48, no. 4, pp. 1798–1807, 1968.
- [9] H. Luo, A. A. Alexeenko, and S. O. Macheret, “Assessment of Classical Impulsive Models of Dissociation in Thermochemical Nonequilibrium,” *J. Thermophys. Heat Transf.*, vol. 32, no. 4, pp. 861–868, 2018.
- [10] M. Panesi, A. Munafò, T. E. Magin, and R. L. Jaffe, “Nonequilibrium shock-heated nitrogen flows using a rovibrational state-to-state method,” *Phys. Rev. E*, vol. 90, no. 1, p. 013009, Jul. 2014.