

Probing Nitrogen Vibrational Relaxation in Hydrogen–Oxygen–Nitrogen Detonations Using Ozone

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1 Introduction

Chemical time scales in detonation systems, e.g., the induction time, are often comparable to the vibrational relaxation time scales of certain gas molecules upon shock impact. Immediately behind a shock wave, molecules require a finite amount of time for their internal degrees of freedom to reach thermodynamic equilibrium, among which the vibrational relaxation processes are the slowest. It has been long speculated that some of the discrepancies between experimental measurements and numerical simulations of detonation cellular structures may result from the use of chemical kinetic models that do not account for the non-equilibrium processes of vibrational relaxation [1].

Previous work has focused on estimating vibrational relaxation time scales of common gaseous species in detonations, and modifying chemical kinetic models to account for the non-equilibrium process of vibrational relaxation. Taylor et al. [2] showed that in H₂–O₂–N₂ mixtures, the ratio of the ignition delay time of the mixture to the vibrational relaxation time of H₂ and N₂ molecules (obtained from [3, 4]) could be in the range of 1 to 10. In such scenarios, numerical simulations that assume instantaneous thermal equilibrium would underpredict the chemical reaction time scales, and thus, potentially explain the underprediction of detonation cell size in H₂–air detonation simulations compared to experimental measurements [1]. Voelkel et al. [5] performed H₂–air detonation simulations with the vibrational relaxation process modeled and showed the non-equilibrium process to play a critical role in determining 2D detonation cell sizes. Shi et al. [6, 7] implemented H₂–O₂ kinetic models that incorporate vibrational non-equilibrium effects and showed an improved detonation cell size prediction against measurements.

To date, there has been limited experimental evidence that supports the need to consider vibrational relaxation in detonation simulation. Zangene et al. [8] performed H₂–O₂ detonation experiments and tune the vibrational relaxation time scales by using two different bath gases – helium and argon. They found an influence of the relaxation effects on the detonation cellular structures, which is most prominent near detonation limits. Despite the relaxation rates can be changed by approximately 50–70% between the two diluent gases, other detonation properties, such as Chapman–Jouguet (CJ) speed and von Neumann (VN) states, also change. Clearly, this makes the data interpretation somewhat difficult, as the difference observed is subject to other system differences such as wall losses during detonation propagation.

In this study, we experimentally probed the effect of vibrational relaxation of N_2 in H_2 - O_2 - N_2 detonations with the assistance of ozone (O_3) doping. We specifically design a range of mixtures aimed at isolating the effect of N_2 vibrational relaxation. The experiments to be reported here aim to 1) provide a mixture design method that allows certain molecular processes to be probed independently, 2) examine the impact of N_2 vibrational relaxation on cellular structures of hydrogen detonations, and 3) identify any potential improvement that is needed for the chemical kinetic model used.

2 Mixture design

For a given initial pressure, two mixture compositions are initially considered. For example, for the initial pressure of 30 kPa, the two mixtures are $2H_2 + O_2 + 3N_2$ and $2H_2 + O_2 + 3O_2$. They are denoted as the nitrogen and oxygen cases, respectively. The two mixtures have approximately the same thermodynamic properties, e.g., CJ and VN states: The mixtures are highly diluted, and as such the burned gas temperature is approximately the same because the extent of product dissociation is not significantly different in spite of the excess O_2 . The two mixtures differ kinetically with the oxygen case giving a fast ignition delay and a shorter induction length (see Table 1). They also differ, evidently, in the vibrational relaxation effect, but because of the kinetic difference, clean isolation of the latter effect is not feasible by considering the above two mixtures only. We therefore introduce a third mixture composed of $2H_2 + O_2 + 3N_2 + 800 \text{ PPMv } O_3$, denoted as the ozonated nitrogen case. This ozonated nitrogen mixture is designed to isolate the vibrational relaxation effect of N_2 while keeping the induction length and post-shock thermodynamic conditions nearly identical to those of the oxygen case. At the level of O_3 doping, the thermodynamic properties remain to be the same as the first two mixtures, but the reaction kinetics is sensitized such that the mixture has the same induction time as the oxygen case, even though it is diluted in N_2 . The comparison between the nitrogen and ozonated nitrogen cases is to show that ozone at a dopant level can drastically alter induction time (or length) without affecting other properties of the underlying mixture [9, 10]. By comparing detonation cell measurements of the three mixtures, we expect to assess the potential impact of N_2 vibrational relaxation in a clean manner.

Three initial pressures and a total of nine mixtures are constructed and tested. All tests are performed at room temperature (300 K). For each initial pressure, the amount of N_2 or O_2 dilution is set to the maximum that allows reliable detonation initiation experimentally. The high dilution minimizes the secondary O_2 effects in the oxygen case (equilibrium perturbation, third-body effects, etc.) and the potential impact of H_2 vibrational relaxation which can be on the same order of magnitude as that of N_2 [2]. According to the vibrational time scale estimations in [2], the current mixture compositions and conditions correspond to ratios of induction time to N_2 vibrational relaxation time in the range of 1 to 3. Therefore, the N_2 vibrational relaxation is expected to play a role in key detonation observables if its effect on the reactive processes is strong.

The complete list of the tested mixtures, their compositions and conditions, is given in Table 1. The list comprises of three sets of mixtures, each at a given pressure. Also shown are the corresponding Zel'dovich–von Neumann–Döring (ZND) detonation calculation results (induction length Δ_i , exothermic length Δ_e , and activation energy E_a as defined in [10]) and experimentally measured cell width λ . The ZND calculations were carried out using the Shock and Detonation Toolbox [11] through Cantera [12], with the FFCM-1 chemical kinetic model [13] combined with the Princeton ozone sub-model [14]. The experiments are carried out in a 36 mm diameter round tube [9, 15]. The uncertainty associated with the numerical simulations is estimated based on the rate parameter uncertainties of the chemical kinetic model [9], while the cell width uncertainty is derived from measurements of over 50 individual detonation cells. Both types of uncertainties represent one standard deviation.

Table 1: Mixture conditions, calculated ZND properties, and experimental measured cell widths.

Case	P (kPa)	Composition	Δ_i (10^{-4} m)	Δ_e (10^{-4} m)	E_a	λ (mm)
30-N ₂	30	2H ₂ + O ₂ + 3N ₂	5.49 ± 0.18	1.65 ± 0.07	6.34 ± 0.09	12.34 ± 2.75
30-N ₂ -O ₃	30	2H ₂ + O ₂ + 3N ₂ , 900 ppm O ₃	2.62 ± 0.09	1.65 ± 0.08	4.71 ± 0.13	5.96 ± 0.89
30-O ₂	30	2H ₂ + O ₂ + 3O ₂	2.62 ± 0.12	0.65 ± 0.04	6.79 ± 0.17	6.82 ± 1.49
40-N ₂	40	2H ₂ + O ₂ + 3.5N ₂	4.80 ± 0.16	1.38 ± 0.04	6.71 ± 0.12	10.06 ± 1.76
40-N ₂ -O ₃	40	2H ₂ + O ₂ + 3.5N ₂ , 800 ppm O ₃	2.24 ± 0.06	1.38 ± 0.05	4.76 ± 0.12	6.31 ± 1.04
40-O ₂	40	2H ₂ + O ₂ + 3.5O ₂	2.25 ± 0.12	0.53 ± 0.03	7.31 ± 0.26	5.85 ± 1.17
50-N ₂	50	2H ₂ + O ₂ + 4.5N ₂	5.46 ± 0.24	1.45 ± 0.06	7.34 ± 0.18	13.67 ± 2.04
50-N ₂ -O ₃	50	2H ₂ + O ₂ + 4.5N ₂ , 500 ppm O ₃	2.50 ± 0.10	1.43 ± 0.06	5.06 ± 0.13	6.81 ± 0.94
50-O ₂	50	2H ₂ + O ₂ + 4.5O ₂	2.49 ± 0.20	0.52 ± 0.03	8.44 ± 0.58	6.94 ± 1.33

Δ_i – induction length, Δ_e – induction length, E_a – activation energy, and λ – cell width.

3 Results and Discussion

Figure 1 shows the temperature profiles from the ZND simulations of the three sets of mixtures. For each set, the nitrogen case has an induction length approximately twice longer than those of the ozonated nitrogen and oxygen cases. Between the nitrogen and ozonated nitrogen cases, the temperature profiles are identical except that the profile in the ozonated nitrogen case is shifted upstream leading to a shortened induction region. Between the ozonated nitrogen and oxygen cases, the induction lengths are equal while the overall temperature profiles are quite similar. Following these ZND simulations, it may be speculated that the difference in the detonation behaviors to be observed for the ozonated nitrogen and oxygen cases is largely attributable to N₂ vibration relaxation effect since everything else is kept nearly the same. Conversely, the two cases would behave similarly if the global impact of N₂ vibrational relaxation is small.

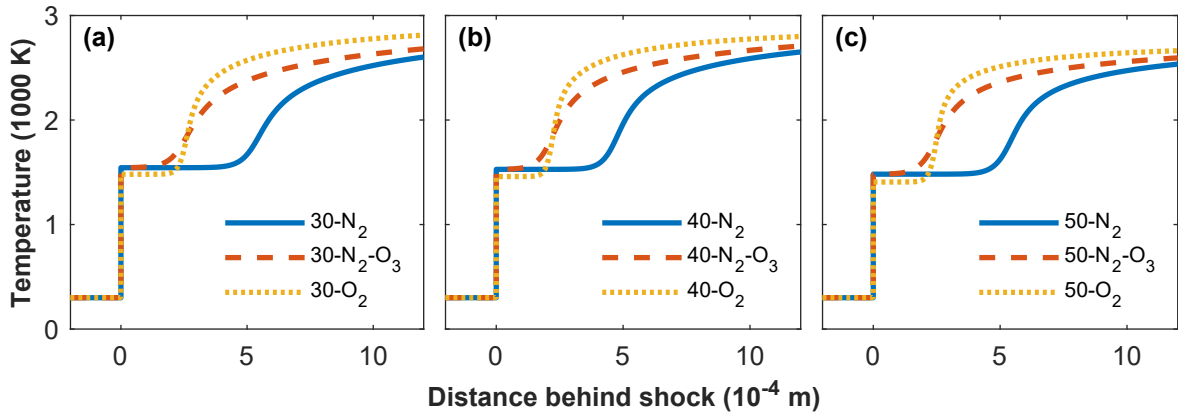


Figure 1: Temperature profiles from ZND detonation calculations. Each subfigure contains the results of the three cases at initial pressures of 30, 40, 50 kPa, respectively.

Experimental soot foils as well as the corresponding cell width measurements are shown in Fig. 2. As expected, the nitrogen case has much larger detonation cells compared to those of the ozonated nitrogen and oxygen cases. Between the ozonated nitrogen and oxygen cases, the cellular structures are found to be quite similar in terms of both the cell width and the visual appearance of the soot foils. Minor differences are observed in cell shapes and clarity, but they are probably the result of inevitable variability in soot foil quality, e.g., soot layer thickness. The current results suggest that

the N_2 vibrational relaxation effect, if any, does not cause notable changes in the detonation cellular structures for the conditions tested, at least within the experimental measurement uncertainty. The same observation holds true for all three initial pressures, which correspond to the VN states varying in temperature from 1400 K to 1600 K and pressure from 8 atm to 13 atm. By correlating the calculated induction lengths and the measured cell widths, as shown in Fig. 3, one can clearly observe that all nine cases lie close to the $\lambda = 25\Delta_i$ line, a long-recognized correlation for hydrogen-based detonations [16]. Again, no noticeable outlier is present for the nitrogen and ozonated nitrogen mixtures.

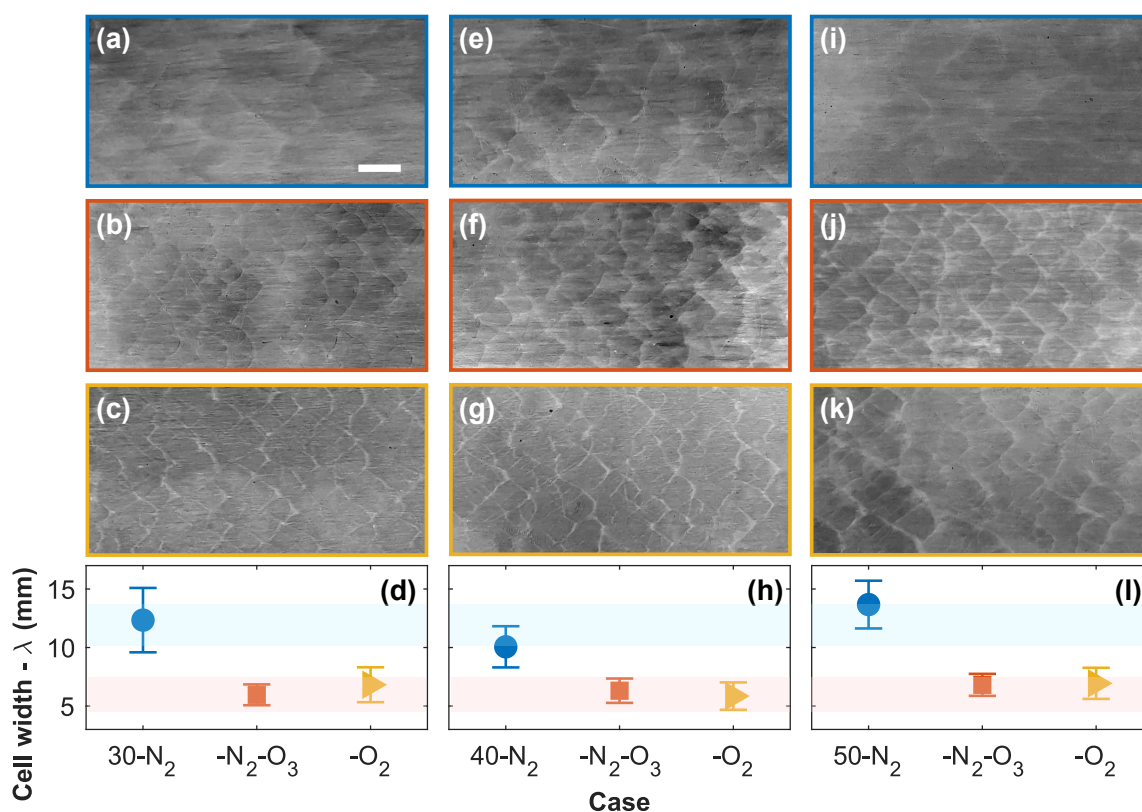


Figure 2: Soot foils and cell width measurements. Each column represents the results of the three cases at initial pressures of 30, 40, 50 kPa, respectively. Scale bar in (a): 10 mm.

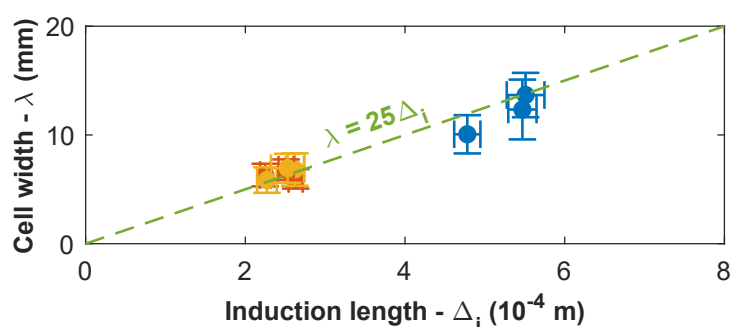


Figure 3: Cell width versus induction length for all nine mixtures.

There are several possible reasons why no impact was observed. First, both the vibrational relaxation and chemical time scales are strong functions of pressure, temperature, and mixture composition. It is possible that under the current conditions N_2 vibrational relaxation time scales are substantially smaller

than the induction time scales. Existing models to estimate relaxation time scales are known not to work very well in mixtures of H_2 [2]. More accurate estimates of the vibrational relaxation time scales may be needed to assess the current results. Second, many of the existing chemical kinetic models are “calibrated” against shock tube measurements. For measurements in H_2 - O_2 - N_2 mixtures with short characteristic reaction time (e.g., ignition delay), the vibrational relaxation effect has already been built into the experimental data, and hence the model itself. Detailed analysis to identify pathways that are most sensitive to vibrational relaxation non-equilibrium processes may help dissect limitations and potential improvement of existing models.

4 Conclusions

We leveraged ozone doping to investigate the impact of the N_2 vibrational relaxation on the global cellular structures of H_2 - O_2 - N_2 detonations. Ozonated N_2 -diluted H_2 - O_2 mixtures are designed to share the same calculated detonation properties as those of corresponding O_2 -diluted mixtures. The corresponding experimental cell measurements show almost identical structures, suggesting that N_2 vibrational relaxation is negligible under the investigated conditions and uncertainty. More accurate estimates of the vibrational relaxation time scales will be performed to identify conditions that are sensitive to vibrational relaxation processes.

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References

- [1] B. Taylor, D. Kessler, V. Gamezo, and E. Oran, “Numerical simulations of hydrogen detonations with detailed chemical kinetics,” *Proceedings of the combustion Institute*, vol. 34, no. 2, pp. 2009–2016, 2013.
- [2] B. Taylor, D. Kessler, and E. Oran, “Estimates of vibrational nonequilibrium time scales in hydrogen-air detonation waves,” in *24th International Colloquium on the Dynamics of Explosive and Reactive Systems, Taipei, Taiwan, July*, vol. 23, 2013, p. 44.
- [3] G. Schott and J. Kinsey, “Kinetic studies of hydroxyl radicals in shock waves. ii. induction times in the hydrogen-oxygen reaction,” *The Journal of Chemical Physics*, vol. 29, no. 5, pp. 1177–1182, 1958.
- [4] D. R. White and R. C. Millikan, “Oxygen vibrational relaxation in o_2 - h_2 mixtures,” *The Journal of Chemical Physics*, vol. 39, no. 8, pp. 2107–2108, 1963.
- [5] S. Voelkel, D. Masselot, P. L. Varghese, and V. Raman, “Analysis of hydrogen-air detonation waves with vibrational nonequilibrium,” in *AIP Conference Proceedings*, vol. 1786, no. 1. AIP Publishing LLC, 2016, p. 070015.
- [6] L. Shi, H. Shen, P. Zhang, D. Zhang, and C. Wen, “Assessment of vibrational non-equilibrium effect on detonation cell size,” *Combustion Science and Technology*, vol. 189, no. 5, pp. 841–853, 2017.

- [7] K. C. Uy, L. Shi, and C. Wen, "Chemical reaction mechanism related vibrational nonequilibrium effect on the zel'dovich- von neumann- döring (znd) detonation model," *Combustion and Flame*, vol. 196, pp. 174–181, 2018.
- [8] F. Zangene, Z. Hong, Q. Xiao, and M. I. Radulescu, "The role of the argon and helium bath gases on the detonation structure of h₂/o₂ mixture," in *International Conference on Hydrogen Safety*, 2021.
- [9] J. Crane, X. Shi, A. V. Singh, Y. Tao, and H. Wang, "Isolating the effect of induction length on detonation structure: Hydrogen–oxygen detonation promoted by ozone," *Combustion and Flame*, vol. 200, pp. 44–52, 2019.
- [10] P. A. Meagher, X. Shi, J. P. Santos, N. K. Muraleedharan, J. Crane, A. Y. Poludnenko, H. Wang, and X. Zhao, "Isolating gasdynamic and chemical effects on the detonation cellular structure: A combined experimental and computational study," *Proceedings of the Combustion Institute*, 2022.
- [11] S. T. Browne, J. L. Ziegler, N. P. Bitter, B. E. Schmidt, J. Lawson, and J. E. Shepherd, "SDToolbox: Numerical Solution Methods for Shock and Detonation Jump Conditions," GALCIT Report FM2018.001, California Institute of Technology, Pasadena, CA, September 2022.
- [12] D. G. Goodwin, H. K. Moffat, I. Schoegl, R. L. Speth, and B. W. Weber, "Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes," <https://www.cantera.org>, 2022, version 2.6.0.
- [13] G. Smith, Y. Tao, and H. Wang, "Foundational fuel chemistry model version 1.0 (ffcm-1)," <http://nanoenergy.stanford.edu/ffcm1>, 2016.
- [14] H. Zhao, X. Yang, and Y. Ju, "Kinetic studies of ozone assisted low temperature oxidation of dimethyl ether in a flow reactor using molecular-beam mass spectrometry," *Combustion and Flame*, vol. 173, pp. 187–194, 2016.
- [15] X. Shi, J. Crane, and H. Wang, "Detonation and its limit in small tubes with ozone sensitization," *Proceedings of the Combustion Institute*, vol. 38, no. 3, pp. 3547–3554, 2021.
- [16] J. H. Lee, "Dynamic parameters of gaseous detonations," *Annual Review of Fluid Mechanics*, vol. 16, no. 1, pp. 311–336, 1984.