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 H\textsubscript{2}–O\textsubscript{2}–N\textsubscript{2} mixtures, the ratio of the ignition delay time of the mixture to the vibrational relaxation time of H\textsubscript{2} and N\textsubscript{2} 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 H\textsubscript{2}–air detonation simulations compared to experimental measurements [1]. Voelkel et al. [5] performed H\textsubscript{2}–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 H\textsubscript{2}–O\textsubscript{2} 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 H\textsubscript{2}–O\textsubscript{2} 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\textsubscript{2} in H\textsubscript{2}–O\textsubscript{2}–N\textsubscript{2} detonations with the assistance of ozone (O\textsubscript{3}) doping. We specifically design a range of mixtures aimed at isolating the effect of N\textsubscript{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\textsubscript{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\textsubscript{2} + O\textsubscript{2} + 3N\textsubscript{2} and 2H\textsubscript{2} + O\textsubscript{2} + 3O\textsubscript{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\textsubscript{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\textsubscript{2} + O\textsubscript{2} + 3N\textsubscript{2} + 800 PPMv O\textsubscript{3}, denoted as the ozonated nitrogen case. This ozonated nitrogen mixture is designed to isolate the vibrational relaxation effect of N\textsubscript{2} while keeping the induction length and post-shock thermodynamic conditions nearly identical to those of the oxygen case. At the level of O\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} or O\textsubscript{2} dilution is set to the maximum that allows reliable detonation initiation experimentally. The high dilution minimizes the secondary O\textsubscript{2} effects in the oxygen case (equilibrium perturbation, third-body effects, etc.) and the potential impact of H\textsubscript{2} vibrational relaxation which can be on the same order of magnitude as that of N\textsubscript{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\textsubscript{2} vibrational relaxation time in the range of 1 to 3. Therefore, the N\textsubscript{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 \(\Delta_i\), exothermic length \(\Delta_e\), and activation energy \(E_a\) as defined in [10]) and experimentally measured cell width \(\lambda\). 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.

<table>
<thead>
<tr>
<th>Case</th>
<th>$P$ (kPa)</th>
<th>Composition</th>
<th>$\Delta_i$ $(10^{-4} \text{ m})$</th>
<th>$\Delta_e$ $(10^{-4} \text{ m})$</th>
<th>$E_a$ (mm)</th>
<th>$\lambda$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30-N₂</td>
<td>30</td>
<td>$2\text{H}_2 + \text{O}_2 + 3\text{N}_2$</td>
<td>5.49 ± 0.18</td>
<td>1.65 ± 0.07</td>
<td>6.34 ± 0.09</td>
<td>12.34 ± 2.75</td>
</tr>
<tr>
<td>30-N₂-O₃</td>
<td>30</td>
<td>$2\text{H}_2 + \text{O}_2 + 3\text{N}_2$, 900 ppm O₃</td>
<td>2.62 ± 0.09</td>
<td>1.65 ± 0.08</td>
<td>4.71 ± 0.13</td>
<td>5.96 ± 0.89</td>
</tr>
<tr>
<td>30-O₂</td>
<td>30</td>
<td>$2\text{H}_2 + \text{O}_2 + 3\text{O}_3$</td>
<td>2.62 ± 0.12</td>
<td>0.65 ± 0.04</td>
<td>6.79 ± 0.17</td>
<td>6.82 ± 1.49</td>
</tr>
<tr>
<td>40-N₂</td>
<td>40</td>
<td>$2\text{H}_2 + \text{O}_2 + 3.5\text{N}_2$</td>
<td>4.80 ± 0.16</td>
<td>1.38 ± 0.04</td>
<td>6.71 ± 0.12</td>
<td>10.06 ± 1.76</td>
</tr>
<tr>
<td>40-N₂-O₃</td>
<td>40</td>
<td>$2\text{H}_2 + \text{O}_2 + 3.5\text{N}_2$, 800 ppm O₃</td>
<td>2.24 ± 0.06</td>
<td>1.38 ± 0.05</td>
<td>4.76 ± 0.12</td>
<td>6.31 ± 1.04</td>
</tr>
<tr>
<td>40-O₂</td>
<td>40</td>
<td>$2\text{H}_2 + \text{O}_2 + 3.5\text{O}_2$</td>
<td>2.25 ± 0.12</td>
<td>0.53 ± 0.03</td>
<td>7.31 ± 0.26</td>
<td>5.85 ± 1.17</td>
</tr>
<tr>
<td>50-N₂</td>
<td>50</td>
<td>$2\text{H}_2 + \text{O}_2 + 4.5\text{N}_2$</td>
<td>5.46 ± 0.24</td>
<td>1.45 ± 0.06</td>
<td>7.34 ± 0.18</td>
<td>13.67 ± 2.04</td>
</tr>
<tr>
<td>50-N₂-O₃</td>
<td>50</td>
<td>$2\text{H}_2 + \text{O}_2 + 4.5\text{N}_2$, 500 ppm O₃</td>
<td>2.50 ± 0.10</td>
<td>1.43 ± 0.06</td>
<td>5.06 ± 0.13</td>
<td>6.81 ± 0.94</td>
</tr>
<tr>
<td>50-O₂</td>
<td>50</td>
<td>$2\text{H}_2 + \text{O}_2 + 4.5\text{O}_2$</td>
<td>2.49 ± 0.20</td>
<td>0.52 ± 0.03</td>
<td>8.44 ± 0.58</td>
<td>6.94 ± 1.33</td>
</tr>
</tbody>
</table>

$\Delta_i$ – induction length, $\Delta_e$ – induction length, $E_a$ – activation energy, and $\lambda$ – 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 $\text{N}_2$ vibration relaxation effect since everything else is kept nearly the same. Conversely, the two cases would behave similarly if the global impact of $\text{N}_2$ 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 \( \text{N}_2 \) 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.

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 \( \text{N}_2 \) 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 H₂ [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 H₂-O₂-N₂ 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 N₂ vibrational relaxation on the global cellular structures of H₂-O₂-N₂ detonations. Ozonated N₂-diluted H₂-O₂ mixtures are designed to share the same calculated detonation properties as those of corresponding O₂-diluted mixtures. The corresponding experimental cell measurements show almost identical structures, suggesting that N₂ 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


