

Analysis of nonequilibrium molecular nitrogen ultraviolet radiation in pure N₂ shockwaves

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This paper presents an analysis of data previously reported from a test series in the Electric Arc Shock Tube Facility for incident shocks composed of pure Nitrogen. The present work focuses on the lowest velocity measured in the test (approximately 7 km/s) where molecular radiation is significant. Analysis of the spectral data with the NEQAIR radiative transport code obtains post-shock trends in temperature and number densities of the states of N₂. The results suggest that chemical, and possibly thermal, equilibrium has not been obtained within the distance/time measured (about 5 cm/120 μ s). In the nonequilibrium region of the shock, differences between rotational temperatures of different species are observed, as well as differences between rotational and vibrational temperatures. Population of rotational states above the dissociation limit is observed to occur over a distance of several cm. Finally, these data suggest that predissociation strongly affects the C³ Π_u state of N₂, leading to a lower measured radiation than predicted. An effective average pre-dissociation rate is shown to produce reasonable agreement under quasi-steady state approximation.

1. Introduction

In the last decade, the Electric Arc Shock Tube (EAST) facility has been widely used to provide experimental data aiming to validate radiative heating models used for atmospheric entry, mostly at velocities above 9 km/s [1]. More recently, an experimental campaign at velocities below 9 km/s and its analysis resulted in a significant improvement of the air kinetic model using new rates found in the literature [2], but discrepancies were still observed, especially for the N₂ second positive system (N₂(C³ Π_u) $\rightarrow$ N₂(B³ Π_g)). Despite these previous studies, the overall uncertainties related to surface heating for lunar return remain around 50% [3]. A more recent experimental campaign at EAST, named test 62, was conducted in pure nitrogen at velocities ranging from 6 to 11 km/s at a freestream pressure of 0.2 Torr to provide more fundamental data on nitrogen [4]. In this campaign, 17 shots were considered exploitable [4]. A previous study [5] analyzed the data obtained at a velocity of 10.3 km/s, where atomic radiation is dominant, and provided spatially resolved density measurements of different states of nitrogen. This paper focuses on experimental data obtained at a shock velocity of 7.15 km/s where molecular nitrogen is expected to be the dominant source of radiation. Different bands were measured in these tests, but this paper mainly focuses on the N₂ second positive system.

2. Approach

A similar approach to the one presented in Ref [5] was used and will be briefly presented. An example of experimental data obtained from test 62 campaign is presented in Figure 1. Measurements contained data from four cameras mounted on four different spectrometers for each shot. For each camera, the data are spectrally and spatially resolved, giving a 3D map of radiance versus these two variables. This paper will focus on results measured by the “Blue” camera 4looking at UV radiation. Horizontal and vertical slices shown in Figure 1 represent the integrated radiance versus the spectral and the spatial variable, respectively. The vertical slices are used to get an estimation of the shock front location.

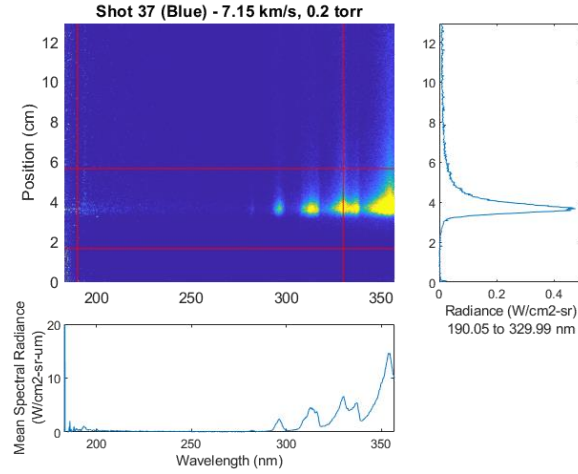


Figure 1: 3D spectral intensity maps obtained for shot 37 at 7.15 km/s with the Blue and Red cameras

In this work, the radiance is binned over the spatial variable to get spectra with a good signal to noise ratio at different positions. As a starting point, the average radiance is binned from 2-7 cm after the shock front. This region will be referred to as the post-shock region in this paper. In order to study the spatially resolved data, the radiance is also binned over 0.5 cm intervals (when not stated otherwise) starting from shock front. This binning interval is chosen as a compromise between having a good signal-to-noise ratio and good spatial resolution. The spectra are then analyzed using the NEQAIR radiation code [4] [6] to get temperatures and species density measurements [5]. NEQAIR can generate the state distribution by assuming a Boltzmann relationship or can solve a reaction kinetic equation for the electronic levels to obtain a non-Boltzmann solution. Both options will be investigated. In this work, the Blue camera is dominated by molecular radiation, and the rotational and vibrational temperatures are fitted independently assuming first $T=T_{\text{rot}}$ and $T_{\text{vib}}=T_{\text{el}}$. While the total density of each species can be inferred from the fits this way, only the density of the excited states responsible for the radiation on a given camera can be measured accurately. The observed transitions and their respective upper and lower levels will be defined in the next sections.

3. Radiation from shocked nitrogen at 7.15 km/s (Shot 37)

On this shot, the wavelength range of the Blue camera measured radiation from 200 to 380 nm. No significant radiation was observed below 280 nm. The spectral data were binned from 2-6 cm behind the shock front to study the post-shock region. The main sources of radiation are the N_2 second positive system, and the N_2^+ first negative system. A comparison between the experimental data, CEA predictions, and the fitted spectra obtained assuming Boltzmann distribution is presented in Figure 2. The contributions of N_2 , N_2^+ , and N^+ to the total radiation are also shown. N^+ was added to the fit to generate continuum bound-free radiation and get an estimate of the electron number density assuming quasineutrality. Other species such as atomic nitrogen and CN were included but did not result in any significant radiation in this region. CEA predictions underestimate the measured radiation, indicating that equilibrium is reached further away from the shock front, as will be discussed.

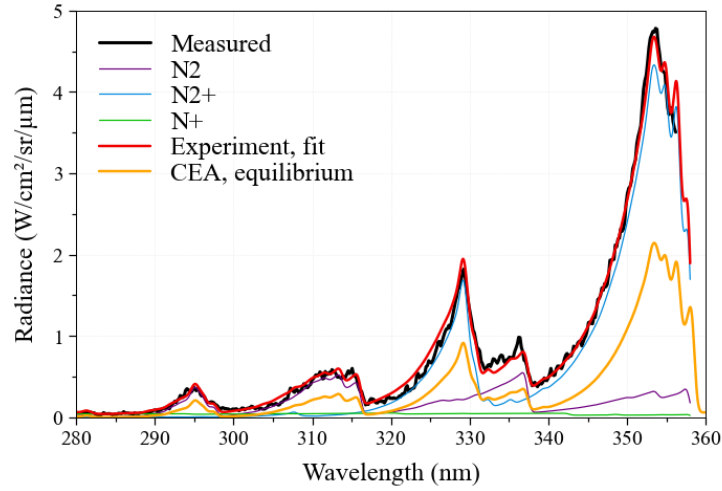


Figure 2: Comparison between the experimental spectrum (black), the spectrum assuming equilibrium conditions computed using CEA (orange), and the best fit spectrum from NEQAIR (red). The individual contributions to the total radiation of each species are also shown.

Table 1: Molecular transitions observed in the experiments. The energies of the upper level of each species are given relative to their ground states.

Name	Transition	Energy of upper level (cm ⁻¹)	Region of emission
N_2 second positive	$N_2: C^3\Pi_u \rightarrow B^3\Pi_g$	89,137	250-450 nm
N_2^+ first negative	$N_2^+: B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	25,461	300-450 nm
CN violet	$CN: B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$	25,753	350-430 nm

Previous studies in shock tubes [7] [8] and a recombining plasma torch flow [9] observed that the rotational temperature of $\text{N}_2^+(\text{B})$ was higher than the gas temperature. To confirm this observation, the experimental spectrum was first fit from 200 to 360 nm, as presented in Figure 2. In that case, most of the radiation comes from $\text{N}_2^+(\text{B})$ and the rotational temperature obtained by fitting the experimental data represents the rotational temperature of $\text{N}_2^+(\text{B})$. (Note that excluding 200-320 nm from the fit resulted in the same fitted temperatures). Then, the spectrum was fit by considering only the radiation from 280 to 320 nm, and from 330 to 340 nm. In these regions, $\text{N}_2(\text{C})$ is the main source of radiation and the fitted temperatures should be representative of the temperatures of $\text{N}_2(\text{C})$. To compute the N_2 second positive system, the spectroscopic constants from Laux [10] were used. Finally, by default, the radiation from all rovibrational levels is computed, including those above the dissociation limit D_0 (quasi-bound levels). An additional fit was performed by ignoring all rovibrational levels of $\text{N}_2(\text{C})$ above its dissociation limit when fitting the $\text{N}_2(\text{C})$ bands. The results on the fitting parameters are given in Table 2 and the comparison of the spectra is presented in Figure 3. The temperature predicted by CEA is lower than the measured temperature for every fit, explaining the underprediction of total radiation in Figure 2. The rotational temperature of $\text{N}_2^+(\text{B})$ is found to be higher than the rotational temperature of $\text{N}_2(\text{C})$. The vibrational temperature of $\text{N}_2^+(\text{B})$ is also found higher than the vibrational temperature of $\text{N}_2(\text{C})$. The vibrational temperature of each species is also found to be lower than any rotational temperature. This was observed consistently for all data analyzed in this paper and will be discussed later on.

Ignoring the radiation from quasi-bound levels (i.e., those that are above the dissociation energy, but below the centrifugal barrier) had no significant impact on the fit results.

Table 2: Comparison of temperatures and densities between CEA predictions and measurements obtained by fitting the Blue spectrum.

	CEA	From $\text{N}_2^+(\text{B})$	$\text{N}_2(\text{C})$ only	$\text{N}_2(\text{C})$ only, quasi-bound levels ignored
Tr	6385.53	7760 ± 60	6700 ± 100	6900 ± 200
Tv		6080 ± 60	4600 ± 100	4400 ± 200
N_2	5.51×10^{16}	$2.7 \times 10^{17} \pm 5 \times 10^{15}$	$2.46 \times 10^{17} \pm 6 \times 10^{15}$	$2.43 \times 10^{17} \pm 7 \times 10^{15}$
N_2^+	4.42×10^{12}	$1.35 \times 10^{13} \pm 1 \times 10^{11}$	$1.84 \times 10^{13} \pm 9 \times 10^{11}$	$2.0 \times 10^{13} \pm 1 \times 10^{12}$
e^-	4.65×10^{13}	$1.22 \times 10^{15} \pm 4 \times 10^{13}$	$1.55 \times 10^{15} \pm 8 \times 10^{13}$	$2.10 \times 10^{15} \pm 4 \times 10^{13}$

Different values of D_0 for $\text{N}_2(\text{C})$ can be found in the literature and are summarized in Ref [11]. The first one, used by NEQAIR15, is $D_0 = 8964.9 \text{ cm}^{-1}$. This dissociation limit comes from the work of Büttenbender and Herzberg [12] who studied the predissociation of $\text{N}_2(\text{C})$ into $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D}^0)$, and their analysis led to this commonly used value [11] coinciding with the energy of $\text{N}(^4\text{S}) + \text{N}(^2\text{D}^0)$. Hori and Undo [13] observed that this predissociation disappeared at higher pressure (around 40,000 Pa) and is replaced by predissociation

through another pathway which allowed the authors to measure levels with energy up to 13627 cm^{-1} . These two predissociation pathways were summarized in detail in the review by Carroll and Mulliken [14]. To summarize, the first value corresponds to the predissociation via the $C'^{5}\Pi$ bound state which has no maximum in its potential curve, leading to a predissociation limit that coincides with the energy of $N(^4S)$ and $N(^2D^0)$. On the other hand, the second pathway at higher pressure occurs via the $C'^{3}\Pi_u$ state which has a maximum in its potential curve [15] at this higher value. Finally, in Ref [10], the value of $D_0 = 28220 \text{ cm}^{-1}$ was proposed and corresponds to the theoretical dissociation limit without taking into account predissociation, i.e., the energy of $N(^2D^0) + N(^2D^0)$. More recent potential calculations, however, suggest this third limit should not apply as the $N_2(C)$ potential curve does not continue to this limit and instead forms an avoided crossing and continues into the C' state, which is a second minima within the same potential curve [16]. That larger D_0 seems then outdated and was not considered here. Three different fits were attempted with the two values of D_0 , and suppressing quasi-bound levels as shown in Figure 3 as well as a fit which include radiation from quasi-bound levels. Similar results were obtained for both D_0 's when including the radiation from quasi-bound levels so only one is presented. These spectra were independently fit and therefore each represents the best agreement with experiment given the constants assumed. The apparent shifting of the (4,2) bandhead of $N_2(C)$ in this case is due to truncation of the rotational sequence. As mentioned, this higher D_0 has been observed at higher pressure (above 40,000 Pa [13], which is reasonably close to the post-shock measurement of 17,000 Pa).

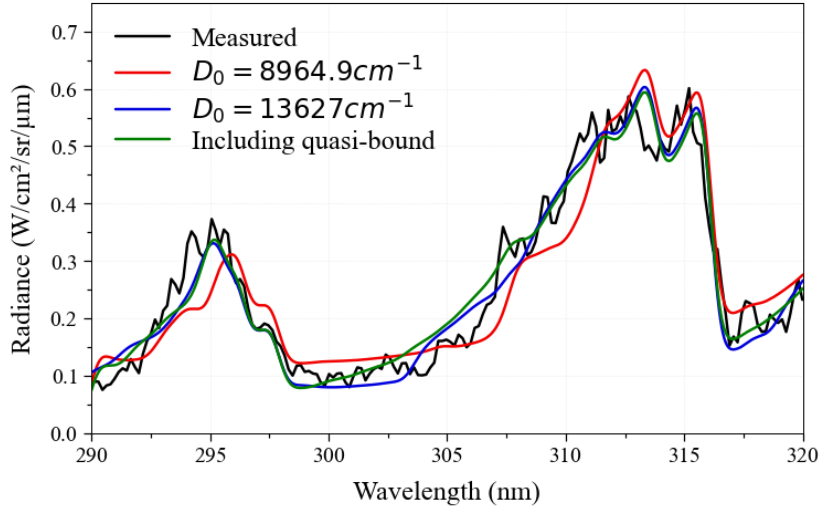


Figure 3: Comparison between the computed spectrum (dashed orange) zoomed over the 290-320 nm region obtained by fitting the Blue experimental data (black) using the spectroscopic constants given by Laux [10] and by ignoring radiation from quasi-bound levels using different values for D_0 . Red: : $D_0 = 8964.9 \text{ cm}^{-1}$ [12] Blue: $D_0 = 13627 \text{ cm}^{-1}$ [13]. Another fit was attempted assuming radiation from quasi-bounds level (green).

The experimental data are next binned over 0.5 cm to obtain spatially resolved spectra. These spectra are then similarly fit to obtain temperatures and density measurements. An additional fit was performed,

considering only the vibrational bands of $N_2(C)$ to assess if the temperatures of $N_2(C)$ and $N_2^+(B)$ were equal. Because the signal-to-noise ratio for $N_2(C)$ radiation drops quite low beyond 1.5 cm behind the shock front, from this point on the spectra were binned over 1 cm to obtain usable data. Results on the rotational and vibrational temperatures are presented in Figure 4. The effect of a Boltzmann or non-Boltzmann distribution as well as the effect of the different options regarding D_0 were studied, but all gave consistent temperatures. The results are consistent with the temperatures measured in the post-shock region. A much lower vibrational temperature of $N_2(C)$ is measured again compared to its rotational temperature. The rotational temperature of $N_2(C)$, which is believed to be more representative of the gas temperature [17], tends to agree with CEA predictions after 3.5 cm which could indicate that thermal equilibrium is reached at this point. The rotational temperature of $N_2^+(B)$ is found to be higher than the rotational temperature of $N_2(C)$ at almost every position. Using the temperature measured by fitting $N_2(C)$ in the post-shock region and the pressure measured by the wall-mounted pressure transducer (17000 Pa), the rotational-translational relaxation timescale (τ_{RT}) can be estimated. The value of τ_{RT} is estimated at 6.2 ns using the rates given by either Parker [18] or Panesi [19] [20]. The lifetimes of $N_2(B)$, $N_2(C)$ and $N_2^+(B)$ in these conditions are found to be 46, 27 and 2.4 ns, respectively, using the rates given in Table 3, assuming that quenching and radiative decay are the main source of species depletion. The lifetimes of $N_2(B)$ and $N_2(C)$ are therefore lower than τ_{RT} and their rotational temperatures can be used to measure the gas temperature [21]. However, τ_{RT} is higher than the lifetime of $N_2^+(B)$ which can lead to a different rotational temperature of $N_2^+(B)$ than the gas temperature.

The differences between the rotational and vibrational temperature of $N_2(C)$ can be found surprising. The T-Tv relaxation time in these conditions should be around or below 1 μ s [22], and thermalization should then be achieved around 1.5 cm behind the shock front. However, as explained in Refs [23] [24], dissociation has an influence on the vibrational relaxation at higher temperature, and dissociation occurs preferentially via high lying vibrational levels [24]. Behind the shockwave, the dissociation of the gas will depopulate the high lying vibrational levels, leading to a smaller measured vibrational temperature. Note that the vibrational temperature should trend to the gas temperature when the dissociation reaction approaches equilibrium. Recent studies [25] [26] measured vibrational temperatures in O_2/Ar shock waves and found a vibrational temperature lower than the gas temperature by 5 to 20% at temperatures ranging from 5000 to 10000 K even 5 cm away the shock front [25]. This discrepancy also suggests that not only is this region in chemical non-equilibrium, but it is also in thermal non-equilibrium. Another reason for the low vibrational temperature could come from the predissociation of $N_2(C, v=4)$ into $N(^4S)$ and $N(^2D^0)$. According to Refs [27] [14], predissociation into $N(^4S^0)$ and $N(^2D^0)$ affects the vibrational level $v = 4$ of $N_2(C)$. This predissociation is also presented in the review by Wright [28] and Anketell [29] as an $N_2(C, v=4)$ population mechanism. Predissociation actually affects every vibrational levels of $N_2(C)$, including the levels below $v=4$, but only at high rotational level J [30]. The predissociation rate of $v=4$ will therefore be higher than the rates for $v<4$. An underpopulation of atomic nitrogen, expected in such compressing flows, will lead to an underpopulation of the $N_2(C, v=4)$ level, which in turn impacts lower vibrational levels by $v-v$ processes. This could lead to a lower effective vibrational temperature of $N_2(C)$, thus explaining the results obtained by fitting the spectra. This will be the focus of the next paragraph when analyzing spatially resolved spectra.

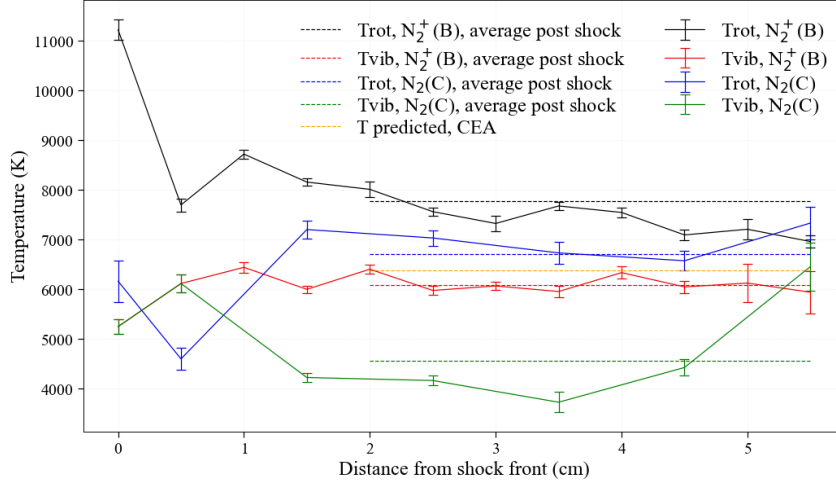


Figure 4: Rotational and vibrational temperature profiles obtained by fitting the spatially resolved spectra of the Blue camera. The temperatures obtained by fitting the Blue spectrum in the post-shock region (dashed lines) are also shown for comparison.

Table 3: Lifetimes estimated in the post-shock region.

	Rate Constant of Quenching by N_2 (10^{-10} cm ³ /s)	Radiative lifetime (ns)	Lifetime in the post- shock region (ns)	τ_{RT} (ns)
$N_2(B)$	0.25 [31]	13500 [10]	46	6.3
$N_2(C)$	0.11 [31] [32]	37 [10] [33]	27	
$N_2^+(B)$	4.6 [32]	60 [10] [34]	2.4	

Finally, the spatially resolved spectra were fit looking only at $N_2(C)$ radiation and using the three different D_0 given above, ignoring radiation from quasi-bound levels. Note that the radiation computed using the larger D_0 gave similar results by including radiation from quasi-bound levels. The comparison between the fitted spectra and the experimental data is presented in Figure 5. The spectra computed using the smallest D_0 [12] gives better agreement up to 2.5 cm from shock front. After that distance, that agreement gets worse, and the spectra computed with the larger D_0 gives a better agreement. A slight difference is observed between the spectra computed with the two larger D_0 with a slightly better agreement using $D_0=13627$ cm⁻¹ [13] in the 300-310 nm region. After 3.5 cm, a feature around 294 nm is observed but not modeled, as reported in [10]. Figure 5 clearly shows that the radiation from higher rovibrational levels of $N_2(C)$ is not observed before 1.5 cm. This could come from predissociation as it does not affect each rovibrational level equally. To test the hypothesis, the predissociation of $N_2(C)$ was added to the non-Boltzmann model of NEQAIR. In Ref [30], rovibrational specific rate constants of $N_2(C)$ predissociation are given for $v=0$ to 7. However, NEQAIR applies global rates for predissociation of each electronic level, using a Boltzmann averaging over vibrational levels. Higher vibrational levels may be suppressed by lowering the dissociation energy of the

state, and quasi-bound rotational levels may be optionally disabled. As pointed out in Refs [12] [13] [11], vibrational levels above $v=4$ are not experimentally observed, due to the fast predissociation of these levels. Furthermore, quasi-bound levels will also be affected by predissociation, and the densities of such levels will be largely underpopulated. Thus, different values of D_0 are explored along with disabling the quasi-bound states to compare against the experimental data.

Based on these results, predissociation via the $^5\Pi$ state [14] strongly affects $N_2(C)$ close to the shock front leading to the depopulation of all quasi-bound levels. The rotational distribution of the lower energy levels of $N_2(C)$ may also be influenced by this fast predissociation but is not discerned from the data. After 2.5 cm, however, radiation from rovibrational levels above the smallest D_0 is observed. The result indicates that mechanisms for populating these levels exceed the rate of predissociation through the $^5\Pi$ state but are still slower than those through the $C'^3\Pi_u$ state. This can be brought on at high pressures, as observed by Hori [13], but also requires sufficient time to populate the lower levels that can be collisionally excited into these states. The overall interpretation of the data is that quasi-bound levels can be ignored for $N_2(C)$, but the appropriate value of D_0 to use depends upon the extent of internal excitation. This could be better predicted using a rotationally and vibrationally specific quasi-steady state (QSS) model with individually prescribed predissociation rates from the different v and J levels of $N_2(C)$, as performed by Mariotto [30]. The simplified approach taken in this work is to compute the $N_2(C)$ predissociation rate assuming densities of quasi-bound levels above $D_0=13627\text{ cm}^{-1}$ are negligible, and levels below this limit follow a Boltzmann distribution. Based on the rates given in Ref [30], vibrational specific rates were computed. While these rates vary with temperature due to changes in rotational populations, they were found to be relatively constant above 5000 K. The corresponding rate of $N_2(C,v=4)$ was found to be $3\cdot 10^{11}\text{ s}^{-1}$ and the rates of vibrational levels $v<4$ were below $5\cdot 10^8\text{ s}^{-1}$. Therefore, only predissociation into $v=4$ was added to NEQAIR, with a rate constant of $3\cdot 10^{11}\text{ s}^{-1}$. This rate is expected to give a good estimate of the predissociation for temperature ranging from 5000-10000 K. Results obtained using NEQAIR with this predissociation rate will be labeled as “NEQAIR, updated QSS”.

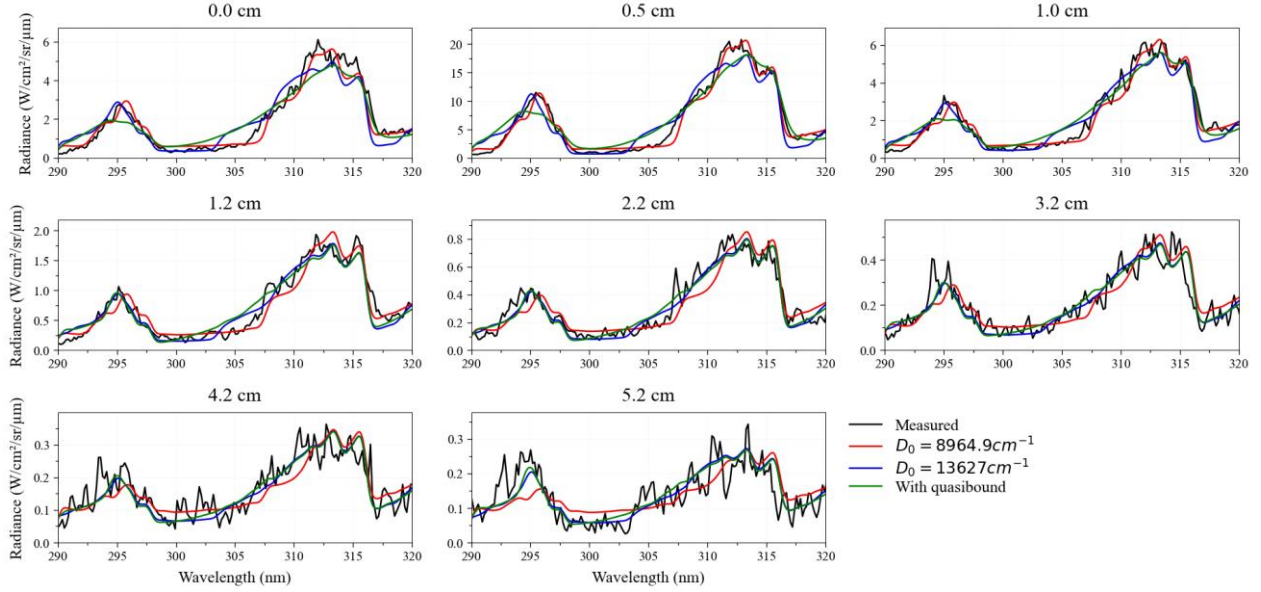


Figure 5: Comparison between fitted spectra computed assuming different values of D_0 (ignoring radiation from quasi-bound levels) and experimental data as a function of the distance from the shock front.

The impact of predissociation on the state distribution of N_2 is demonstrated by producing a Boltzmann plot of all the electronic states of N_2 . The N_2 total density was estimated using additional measurements with the VUV and Red cameras [35], leading to a value of $1.4 \pm 0.2 \times 10^{17} \text{ cm}^{-3}$, assuming a temperature of 6700 K. The densities of $N_2(B)$ and $N_2(a,b,b')$ were measured by fitting the Red and VUV spectra, respectively, in a similar way as presented above for $N_2(C)$. The b,b' measurements are at similar level to noise on the VUV camera so have large uncertainty. Figure 6 presents the comparison between the measured molecular nitrogen population distribution and CEA and non-equilibrium predictions. Every measured state of N_2 is higher than CEA predictions because the shock is not in chemical equilibrium. The Boltzmann distribution computed at the gas temperature based on the rotational temperature of $N_2(C)$ and estimated total molecular nitrogen density is also plotted for comparison. This distribution agrees relatively well with $N_2(a)$ and $N_2(B)$. Simulations with the updated QSS model shown in Figure 6 show the underpopulation of $N_2(C)$ may be attributed to predissociation. Note that the b and b' states of N_2 are not solved explicitly in the non-Boltzmann calculation and are instead assumed to be equilibrated with the a state. The a state density predicted by QSS is close to the Boltzmann values, in good agreement with the measurements.

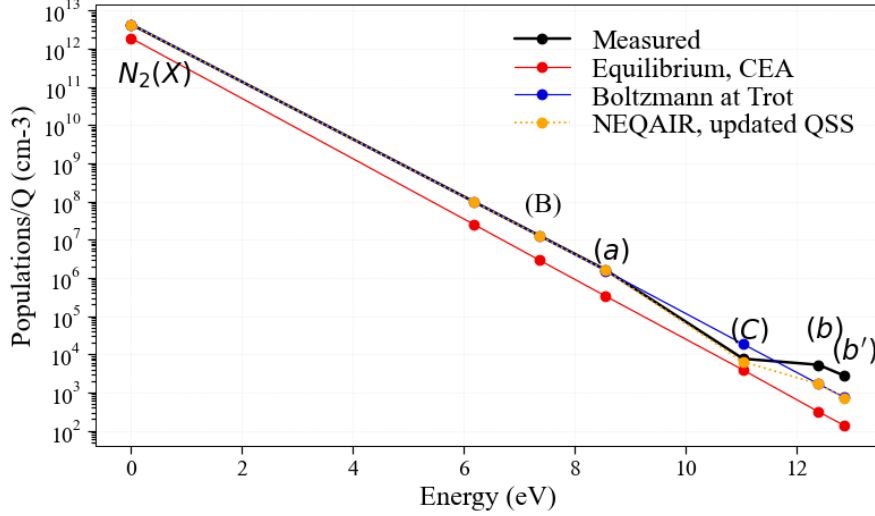


Figure 6: Comparison of the molecular nitrogen population distribution obtained using CEA predictions and by fitting the spectra of the VUV camera. The Boltzmann distribution computed at Trot of $N_2(C)$ is also shown.

Predissociation was only added for the level $v=4$ of $N_2(C)$ in NEQAIR but still affects every rovibrational level. The predissociation rate averaged over $v=4$ was $3 \cdot 10^{11} s^{-1}$ which is faster than the RT rate presented in Table 3. In Table 4, vibrational specific lifetimes of $N_2(C)$ were computed when taking into account vibrational specific predissociation rates. These rates were computed the same way as presented before: the rate is averaged over all rotational levels lower in energy than $D_0=13627 \text{ cm}^{-1}$ within a given vibrational level, using the rates given in Ref [30]. To simplify, the rates were computed at 7000K. Only the lifetime of $v=0$ is not impacted by predissociation while the lifetimes of $v=1$ and 2 are significantly lower but remain above the RT characteristic time. The lifetimes of level $v=3$ and above become lower than the RT time and the rotational temperature measured using these levels may not represent the gas temperature. The very short lifetimes for $v=4$ and $v=5$ could also indicate that these levels are unlikely to be populated, however as suggested by Fig. 5, inverse processes become important later in the shock. These rates are averaged over every rotational level but predissociation is highly dependent on the considered rotational number. In Table 4, the rotational number above which the rovibrational specific predissociation rate becomes higher than the RT rate divided by 3 is given. Roughly, the rotational level with lower J could be considered thermalized with the gas bulk, while the levels above are not. The first 50 rotational levels of $v=4$ are expected to be thermalized, increasing to 96 for $v=0$. In this paper, the rotational and vibrational temperature was obtained by fitting the (1-0), (2-1), (3-2), (4-3). (2-0), (3-2) and (4-2) bands of the N_2 second positive system. The distributions of levels 3 and 4, in particular, could have been distorted by predissociation. While the real effect on our measurements remains unclear without more investigation, it could explain the lower vibrational temperature as higher vibrational level will be more impacted by predissociation. These results also suggest that gas temperature measurement using $N_2(C)$ should preferentially be performed looking only at vibrational bands emitting from $v < 2$.

Table 4: Comparison between vibrational specific predissociation rates and lifetimes estimated in the post-shock region.

		Predissociation rate at 7000 K (s ⁻¹)	Lifetime accounting predissociation (ns)	Lifetime ignoring predissociation (ns)	τ_{RT} (ns)	J above which	
						E(J,v)> D ₀	k _{pred} (J,v) >k _{RT} /3
N ₂ (C)	v=0	4 · 10 ⁵	27	27	6.3	88	95
	v=1	8 · 10 ⁶	22			81	92
	v=2	4 · 10 ⁷	13			75	78
	v=3	3 · 10 ⁸	3			68	66
	v=4	3 · 10 ¹¹	0.003			60	50
	v=5	9 · 10 ¹¹	0.001			52	30

Finally, the spatial density profile of N₂(C) can be obtained from the fits presented in Figure 5. The density of N₂(C) can also be computed assuming Boltzmann or non-Boltzmann distribution at the temperature measured using N₂(C) only (see Figure 4). Figure 7 shows the comparison of N₂(C) density from the updated non-Boltzmann model including predissociation. The non-Boltzmann model predicts very well the density of N₂(C) after 2 cm. The disagreement at shorter distance is attributed to errors in the measured rotational temperature of the gas presented in Figure 4 and the depopulation of high rovibrational levels of N₂(C) discussed above. The density profiles of N₂(X), N₂(a), N₂(b) and N₂(b') are also presented. The densities of N₂(X) were obtained from the atomic nitrogen measurements presented in Ref [35]. For these states, the QSS model predicted a density equal to equilibrium at the rotational temperature, and therefore only one distribution is plotted. Overall, the density of N₂(a) seems relatively well predicted. N₂(b') however is overpredicted by about one order of magnitude. This is consistent with the observations made with the post-shock region spectrum. Finally, N₂(b) seems overpredicted early in the shock, but tends to agree with the measured density after 3 cm.

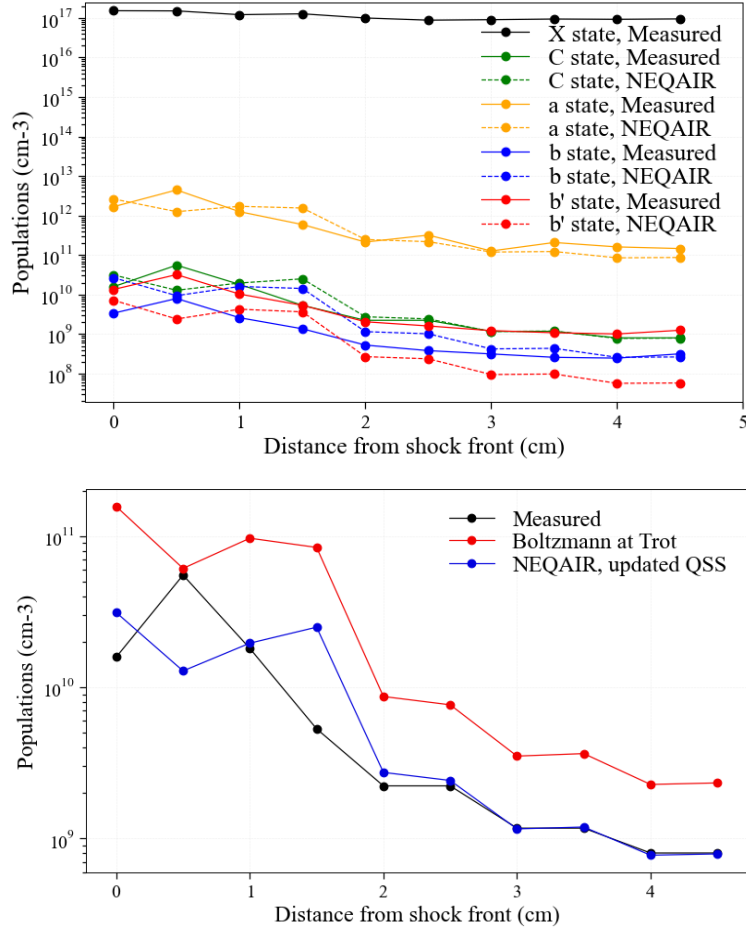


Figure 7. Top: Comparison between measured and computed $N_2(X)$, $N_2(a)$, $N_2(C)$, $N_2(b)$ and $N_2(b')$ distributions resulting from the QSS model. Bot: Comparison between only the measured (black) and computed $N_2(C)$ densities assuming Boltzmann distribution (Red) or resulting from the updated QSS model.

4. Conclusion

An analysis of the radiation of pure nitrogen measured in relatively low shock speed at 7.15 km/s was presented. The radiation measured in the post-shock region is above that which would be predicted at equilibrium by CEA. The analysis of the spatially resolved spectra indicates that chemical equilibrium may be reached after 6 cm from shock front, which corresponds to the limit of the test time for this measurement. The measurements are consistent with the behavior of a compressing flow in that molecular densities peak near the shock front, then decrease at further distances as dissociation occurs. The densities of each molecular state, measured individually, then tend to decrease toward their equilibrium densities predicted by CEA farther from the shock front.

$N_2(C)$ was consistently found to be underpopulated compared to the Boltzmann distribution at the gas temperature and compared to other excited states of N_2 . This was attributed to predissociation which affects the level $v=4$ of $N_2(C)$. The NEQAIR non-Boltzmann model was updated to account for this process, using a rate of $3 \cdot 10^{11} s^{-1}$. This predissociation is fast and decreases the density of all vibrational levels of $N_2(C)$ through v-v excitation. It is observed that, early in the shock, the pre-dissociation prevents population of rovibrational states above the pre-dissociation limit. This depopulation can be modeled by using a lower D_0 in the spectroscopic model and neglecting quasi-bound states. However, after a few centimeters, these levels become populated and the value of D_0 needs to be raised to correspond to the dissociation barrier of the C' state. At present, an accurate prediction of this transition may require a rovibrational specific QSS on $N_2(C)$, but the impact is likely small on the total gas radiation, such that the effective D_0 and pre-dissociation rates can be applied for re-entry applications.

The rotational temperature inferred from fitting the N_2^+ first negative system yields higher values than those obtained from the N_2 second positive systems indicating a higher rotational temperature of $N_2^+(B)$ compared to $N_2(C)$. This was previously observed in shock tubes [7] [8] and a plasma torch facility [9] but also in other plasma sources at lower enthalpy [21] [36]. Based on comparison with R-T relaxation and as explained in Ref [9], the gas temperature is expected to be equal to the rotational temperature of $N_2(C)$. The vibrational temperature of $N_2^+(B)$ was found to equilibrate with the gas temperature within a few cm. The vibrational temperature of $N_2(C)$ remained significantly lower than either temperature, which is attributed to the pre-dissociation of the state.

Acknowledgments

Augustin Tibere-Inglesse's research was supported by an appointment to the NASA Postdoctoral Program at the NASA Ames Research Center, administered by Oak Ridge Associated Universities under contract with NASA. Brett Cruden is supported by NASA contract NNA15BB15C to Analytical Mechanical Associates, Inc. This work was supported by the Entry Systems Modeling project.

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