A study of background emissions enhancements in nitrogen afterglows, due to addition of discharged O_2, in connection with the reactions $\{N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon) + O(^3P)\}$, $\{O_2 \ (a \ ^1\Delta g) + N(^4S)\}$ and $\{O_2 \ (a \ ^1\Delta g) + N_2 \ (A \ ^3\Sigma_u^+)\}$

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Abstract: Intensity enhancement due to the addition of discharged O_2 is examined for background N_2 $(B \ ^3\Pi_g \rightarrow A \ ^3\Sigma_u^+)$ emissions in various flowing nitrogen afterglows. Possible implications are reported for the experimentally determined rate constants for the reactions $\{N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon) + O(^3P)\}$, and $\{O_2 \ (a \ ^1\Delta g) + N(^4S)\}$, as a result of the present study. The present, as well as previously reported, N_2 $(B \ ^3\Pi_g \rightarrow A \ ^3\Sigma_u^+)$ emissions intensity enhancements suggest complementary conclusions. Previous differences in experimental results reported for the $\{O_2 \ (a \ ^1\Delta g) + N(^4S)\}$ reaction [based on studies observing the decay of either O_2 $(a \ ^1\Delta g)$ molecules or $N(^4S)$ atoms alone] are reconciled by a unifying additional interpretation. This interpretation leads to a rate constant estimate for the energy transfer reaction, $\{O_2 \ (a \ ^1\Delta g) + N_2 \ (A \ ^3\Sigma_u^+)\}$, deduced to account for the above N_2 $(B \ ^3\Pi_g \rightarrow A \ ^3\Sigma_u^+)$ emissions intensity enhancements.

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1   Introduction

Because of the great significance of active nitrogen and oxygen for natural processes and various applications on Earth and in space, *many* investigations of these systems have been performed[1-12]. Recently it was reported [10-12] that enhancements of the background N_2 first positive band system (1pbs) [i.e., N_2 (B $^3\Pi_g \to$ A $^3\Sigma_u^+$)] emission intensities in a flowing afterglow of active nitrogen, [henceforth called "N_2 (B→A) increases"], were observed in the form of an orange flame visible even to the naked eye with the laboratory lights on. These enhancements occurred when a stream of microwave (mw) discharged O_2 was mixed with a stream of mw discharged nitrogen without a catalyst and at much higher pressures than ever before [10-12]. The recently studied enhancements, as well as those in previous studies [13,14,15], were uniformly ascribed, in references [10-12], to the interaction between excited N_2, (also described as N_2^* for electronically excited N_2, and as $N_2^\clubsuit$ for vibrationally excited N_2, respectively), and electronically excited O_2, (also O_2^*), that led to collisional intersystem crossing into the N_2 (B$^3\Pi$g) state [10]. On the basis of the available evidence, the N_2 (A $^3\Sigma u^+$) state was explicitly included [10, 12], contrary to its specific exclusion [5]. The term 'intersystem crossing' was used in the looser, more general sense of previous work [16]. The mechanism responsible for the formation of the observed flame was not completely established.

The purpose of this work is to establish the mechanism under question by further examining background emissions in nitrogen afterglows, enhanced by the addition of discharged O_2, in connection with the reactions {N_2 (A $^3\Sigma_u^+$, υ) + O(^{3}P)} and {O_2 (a $^1\Delta g$) + N(^{4}S)}, previously studied [1-9,17].

It should be noted that the collisional energy transfer that leads to this N_2 1pbs background emission enhancement in a nitrogen afterglow can also occur in the upper atmosphere. Investigation of the phenomenon is therefore needed because an understanding of this energy transfer may contribute to the extension of present knowledge of the upper atmosphere, and in various other research areas. Reaction kinetics and dynamics, chemical laser excitation, and simulation modeling of electrical discharges and of excited N_2 upper atmospheric emissions (e.g., in airglow, auroras, red sprites), due to energy transfer from photoelectrons generated by solar ionizing radiation, are some of the research areas affected by this energy transfer.

Quite a few investigations over the past 40 years, including some recent ones, have reported experimental values [1-9]: i) of the rate constant for the overall reaction between the well-known, energy-rich, metastable N_2 (A $^3\Sigma_u^+$) molecules and O(^{3}P) atoms; and ii) of the state specific rate constant for the reaction {N_2 (A $^3\Sigma_u^+$, υ) + O(^{3}P)}, henceforth called reaction AO, for $\upsilon = 0 - 7$. None of these studies has taken into account any possible effects of the observed "N_2 (B→A) increases" [10-12] on these experimental chemical reaction rate constants. Similar "N_2 (B→A) increases" were reported [13-14] in the 1960s. The "N_2 (B→A) increases" were initially ascribed to such factors as the effect of O(^{3}P) atoms on the vibrational redistribution of N_2 (B $^3\Pi_g$) via formation of N_2 (A $^3\Sigma_u^+$), that collisionally crosses into the N_2 (B $^3\Pi_g$) state [10-14]. N_2 (A $^3\Sigma_u^+$) was assumed

to be produced either catalytically [14], due to surface-catalyzed formation of excited NO, in early work, and, in later work due to N atom recombination by the $O(^3P)$ atom-conditioned surface; or without a metallic catalyst [13].

The scientific literature includes differing interpretations as far as the reaction AO is concerned. In an early article [13], for example, (increased) formation of N_2 (A $^3\Sigma_u^+$) molecules was assumed to account for the effect of $O(^3P)$ atoms on the vibrational redistribution of N_2 (B $^3\Pi_g$) in an afterglow of active nitrogen formed by DC discharging N_2. It was supposed that efficient ground state N atom recombination assisted by $O(^3P)$ as a third body would lead to vibrationally excited N_2 (A $^3\Sigma_u^+$, v), that would in turn cross into the N_2 (B $^3\Pi_g$) state. But later work by others [2-5] reported destruction of N_2 (A $^3\Sigma_u^+$) molecules as a result of the reaction AO. In fact, even the involvement of N_2 (A $^3\Sigma_u^+$) molecules in the "N_2 (B→A) increases" had been explicitly excluded [5], as pointed out in references 10-12. In addition, there have been disagreements regarding the cause of the O_2 (a $^1\Delta g$) decay [10,17] and the reactivity of N atoms [17] in the assumed reaction $\{O_2$ (a $^1\Delta g$) + N$\}$, henceforth called reaction aN, which will be further reconsidered in this work.

The extreme complexity of the field investigated (as a referee for this paper phrased it) has led to various discrepancies over the years, often arising from the need for tentative assumptions in attempts to explore the unknown. The present work is somewhat retrospective. Supported by an extensive survey of the available, broad, pertinent scientific literature, it is also trying to present unifying arguments that can resolve the discrepancies. These arguments lead to reconciliation of previous conclusions and to refutation of some other conclusions in the light of the new experimental findings for the system studied: background emissions enhancements in nitrogen afterglows, by adding discharged oxygen, that can lead to a flame. The present investigation critically examines new and previous [1-12] data from extensive research on emissions and energy transfer in a flowing afterglow of active nitrogen and oxygen, when discharged O_2 is added to it. It reports on an analysis of previous experiments [2,13] on enhanced spectra; and on unifying arguments about the role of possible nitrogen and oxygen species in the "N_2 (B→A) increases". A unifying mechanism is also deduced for the "N_2 (B→A) increases" caused by discharged O_2, both with and without a catalyst, previously reported [10-14]. The present studies of "N_2 (B→A) increases" caused by discharged O_2, that led to the appearance of a flame, started with higher nitrogen pressures[10] than any in previous works. The implications of the "N_2 (B→A) increases" are considered for chemical reaction studies (for chemical kinetics, and applications such as discharges and active media for lasers) and for upper atmospheric emissions. A kinetic analysis is also presented of data obtained in this investigation and of previously published data for the aN reaction [17]. An interpretation of the mechanism of the aN reaction is presented that reconciles the previous conflicting conclusions about it: namely, that the observed O_2 (a $^1\Delta g$) decay [10,11,15,17] is due to reaction with N_2 (A $^3\Sigma_u^+$), rather than with N atoms. This interpretation is in agreement also i), with the N_2 (A $^3\Sigma_u^+$) decay by O atoms (actually by discharged O_2), repeatedly observed in the study of the reaction AO[1-9]; and ii), with the reported non-reaction of

N atoms with O_2 (a $^1\Delta g$) [17]. Data from the N_2 (A $^3\Sigma_u^+$) and O_2 (a $^1\Delta g$) decays are used to estimate a rate constant for the implied reaction {O_2 (a $^1\Delta g$) + N_2 (A $^3\Sigma_u^+$)}, henceforth called reaction aA. Figure 1 shows
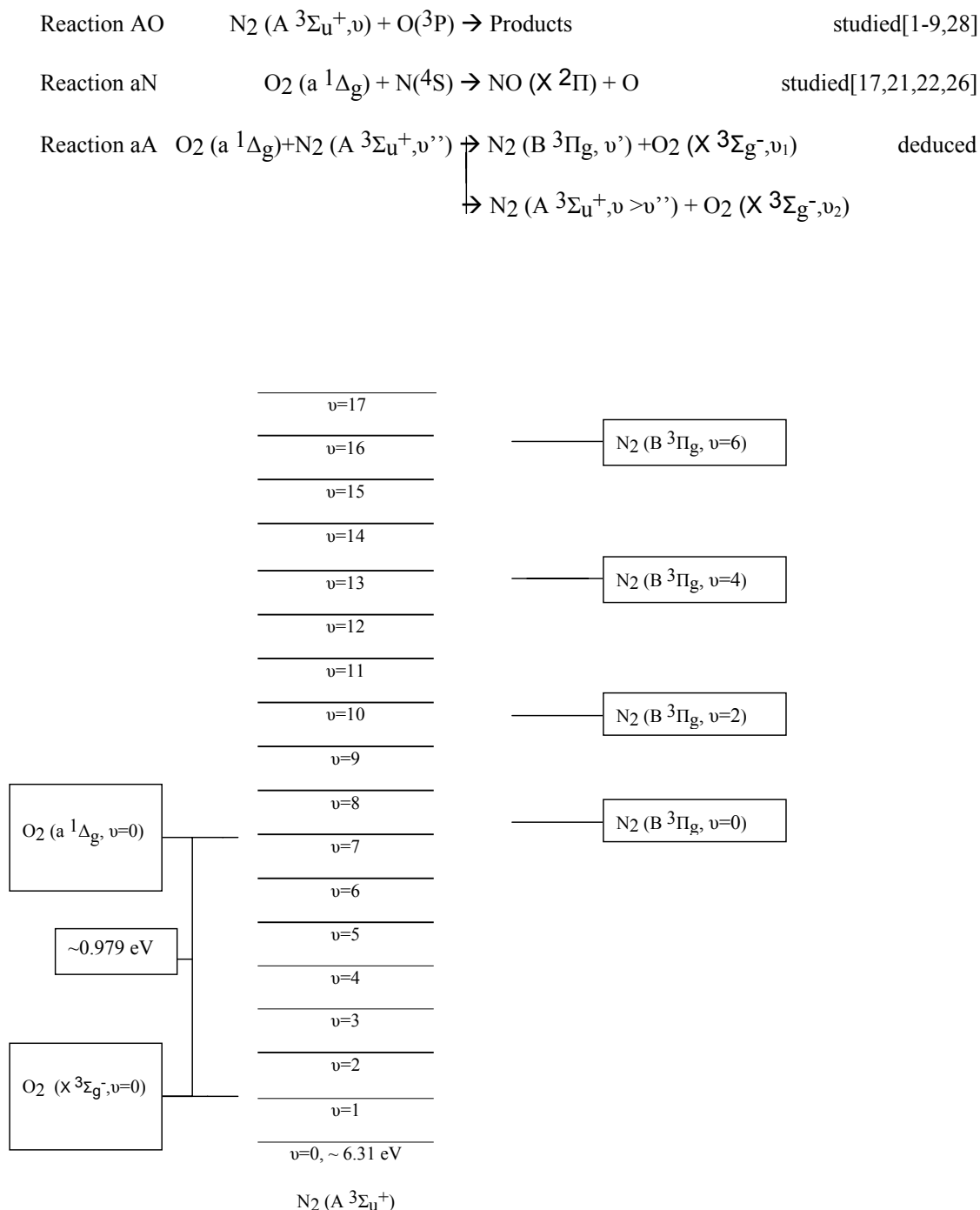
Reaction AO N_2 (A $^3\Sigma_u^+$,υ) + O(^{3}P) → Products   studied[1-9,28]

Reaction aN O_2 (a $^1\Delta_g$) + N(^{4}S) → NO (X $^2\Pi$) + O   studied[17,21,22,26]

Reaction aA O_2 (a $^1\Delta_g$)+N_2 (A $^3\Sigma_u^+$,υ'') → N_2 (B $^3\Pi_g$, υ') +O_2 (X $^3\Sigma_g^-$,υ$_1$)   deduced

                                              → N_2 (A $^3\Sigma_u^+$,υ >υ'') + O_2 (X $^3\Sigma_g^-$,υ$_2$)

Fig. 1 A schematic diagram of vibrational energy levels of the first excited –metastable- electronic N_2 state, N_2 (A Σ_u^+), that is energy rich (~6,31 eV over the ground state energy for υ =0), and of the higher N_2 (B $^3\Pi_g$) electronic state, and of the potential energy difference between the first excited –metastable- electronic O_2 state, O_2 (a $^1\Delta g$,υ=0), and the ground electronic O_2 state, O_2 (X^3 Σ_g^-,υ=0), with the same energy scale. The 3 reactions considered in this work are shown on the top of the diagram.

the reactions considered in this study. It also shows vibrational energy levels of the energy rich ($\sim$6,31 eV over the ground state energy for $\upsilon = 0$), first excited (metastable), electronic state of N_2, N_2 (A $^3\Sigma_u^+$), and of the higher electronic state, N_2 (B $^3\Pi_g$). The potential energy difference between the first excited (metastable) electronic state of O_2, O_2 (a $^1\Delta g$, υ=0), and the ground electronic state, O_2(X $^3\Sigma_g^-$,υ=0) is also depicted in Figure 1.

N$_2$ (A $^3\Sigma_u^+$), an energy rich metastable molecule, is a well-known energy donor to nitrogen and non-nitrogen species. Nevertheless, the evidence reported below indicates that N_2 (A $^3\Sigma_u^+$) is also an efficient energy acceptor from non-nitrogen species: in particular, from excited O_2. An estimate of the pertinent reaction rate constant is also obtained. The evidence in this study strongly suggests that the N_2 (A $^3\Sigma_u^+$, υ) decay[1-9] reported in all of the studies of the reaction AO, and the O_2 (a $^1\Delta g$) decay reported in the studies of the reaction [17] aN and in the studies of the observed "N_2 (B$\rightarrow$A) increases" [10,11,15], are predominantly due to the proposed energy transfer reaction aA. Evidence in this work indicates that the energy transfer reaction aA leads to the reported orange flame [10-12]. Previous values of rate constants for the reactions AO and aN were determined by monitoring the decay of a single reactant under pseudo unimolecular conditions: Either the N_2 (A $^3\Sigma_u^+$,υ) [1-9] or the O_2 (a $^1\Delta g$) [10,11,15,17] decay. The estimate of the rate constant for the reaction aA, deduced in this work, is based on additional evidence, as shown below.

2 Experimental section

Experiments have been done to investigate the effect of active oxygen on the "N_2 (B$\rightarrow$A) increases" in various nitrogen afterglows, and to explore possible effects on the experimentally determined rate constants for the reactions AO and aN. The experimental apparatus consisted of a conventional cylindrical flow reactor system (of 3,4 and 4,8 cm i.d.). O_2 and N_2 – either with or without Ar- were allowed to flow into a Pyrex flow tube through two separate side-arms, where two microwave (mw) discharges – using common diathermy units – could produce active nitrogen and oxygen, respectively. Observations at room temperature (300 K) were made normal to the flow tube with Ebert-Fastie and Czerny-Turner type spectrometers, photomultipliers with S-20, S-5 and 605s photocathodes spanning the near UV and the visible range. A grating blazed in the first order at 600 nm was used. Gas flows in the range of 3-10 bar cm^3/s were used. The apparatus is described in detail in reference [10].

3 Results and discussion

"N$_2$ (B$\rightarrow$A) increases", observed in this work as the result of adding mw discharged O_2 in various flowing nitrogen afterglows are shown in Figures 2-4.

In order to deduce the mechanism of the energy transfer that causes the "N_2 (B$\rightarrow$A) increases", and assess its possible effect on the reactions aN and AO, the results of the

present study must be considered in conjunction with those from earlier studies. Of particular importance are i). O_2 (a $^1\Delta g$) concentration decay due to discharged nitrogen observed by this author [10,11,15] and by others [17], and ii). N_2 (A,$v = 0-7$) concentration decay due to discharged oxygen [1-9].

The studies of the reaction AO [1-9] for $v = 0-7$ were done by monitoring the decay of the N_2 (A $^3\Sigma_u^+$) species either through the weak N_2 (A $^3\Sigma_u^+ \to X\ ^1\Sigma_g^+$) (Vegard-Kaplan) emissions [3-6], or through laser induced fluorescence (LIF) [1,2,8] in a flowing nitrogen afterglow. N_2 (A $^3\Sigma_u^+$) species were generated: i), by pulsed RF discharging N_2-O_2 mixtures [1,8]; ii) by using reactive collisions of Ar metastable species ($^3P_{0,2}$) and N_2, thus forming N_2 (C $^3\Pi_u$) species primarily, that quickly cascade to N_2 (A $^3\Sigma_u^+$) species via the N_2 (B $^3\Pi_g$) state [3-5]; and iii), by flowing Ar + $\sim$0.7% N_2 through a DC discharge, and by reacting discharged (Ar + 0.1 % Xe) –by passing it through a DC discharge– and N_2 in reference [2].

Reference [2] also reports an interesting "too large" increase in the background emission intensity in the study of the reaction AO, compared to the background emission intensity in the study of the reaction $\{N_2$ (A $^3\Sigma_u^+$, v) + $O_2\}$ previously studied. The background emission with the anomalously large magnitude was presumed, in reference [2], to result from "red" singlet (b $^1\Sigma$) and "dimol" (a $^1\Delta$) O_2 emissions. In references [2-4] O(^{3}P) was generated by mw discharging O_2 in (He $- O_2$) [2-4] or (Ar $- O_2$) [2] mixtures. Thus O_2^* was also expected to be present in the stream of discharged O_2 employed; because O_2^* is formed along with O in the O_2 mw discharge zone. So N_2^* as well as O_2^* species are present in the system of the flowing afterglow of active nitrogen in reference [2]. The anomalously large magnitude of the background emission in reference 2 should therefore be considered further, since it could be the result of "N_2 (B→A) increases" [10-12]. "N_2 (B→A) increases" could affect the accuracy of the rate constants determined for the reaction AO for $v = 0-7$, because of the extraneous change caused – e.g., by N_2 (B $^3\Pi_g \to A\ ^3\Sigma_u^+$) emissions, that generate N_2 (A $^3\Sigma_u^+$) – in the N_2 (A $^3\Sigma_u^+$) concentration, as shown below. The N_2 (A $^3\Sigma_u^+$) concentration is employed in the determination of AO reaction rate constants.

It should be noted that if the background emission in reference [2] had also been investigated with the nitrogen discharge off, and a signal could have been observed, then the magnitude of any contribution to the emissions intensity from "red" singlet (b $^1\Sigma$) and "dimol" (a $^1\Delta$) O_2 from the discharged oxygen would have been larger, because there could have been no formation of energetic nitrogen species (e.g., N and N_2^*) species capable of quenching "red" singlet (b $^1\Sigma$) and "dimol" (a $^1\Delta$) O_2 in the absence of the nitrogen discharge. In that way "red" singlet (b $^1\Sigma$) and "dimol" (a $^1\Delta$) O_2 emissions would have been established and there would have been no need to presume them [2]. There is no reference to such a procedure. Apparently either O_2^* emissions from the discharged oxygen with the nitrogen discharge off were not checked, or they were checked and no signal was observed. Thus, what was observed was an anomalously intense background emission with both discharges on, that was presumed in ref. [2] to be "red" singlet (b $^1\Sigma$) and "dimol" (a $^1\Delta$) O_2 emissions, as if they resulted via energy transfer from activated

nitrogen to O_2^*, which, subsequently, emitted radiation.

In any event, if the presumption of reference [2] is correct, emission bands at the wavelength of the "red" singlet (b $^1\Sigma$) and "dimol" (a $^1\Delta$) O_2 emissions ought clearly to be apparent in the spectra so far obtained. No such emission bands were observed at these wavelength ranges in the spectra of the present and of previous [10-13,15] investigations. Of course it is well known that, as a result of the different methods of N_2 (A $^3\Sigma_u^+$) generation, there are very many fewer N atoms in the "cleaner" systems of references [3-6] (even of reference [2]) where N_2 (A $^3\Sigma_u^+$) has been considered to be practically the sole electronically excited N_2 species, than in the very complex systems of references [10-13], where active nitrogen was generated by discharging N_2. The aforesaid observations: i), about the absence of "red" and "dimol" singlet O_2 emissions, and ii), about nitrogen afterglows with fewer forms and numbers of energetic nitrogen species will provide evidence later in this article, in order to further support the involvement of N_2 (A $^3\Sigma_u^+$) in energy transfer with O_2 (a $^1\Delta g$) to produce "N_2 (B→A) increases" that can lead to the reported flame [10-12].

In order to further investigate the "N_2 (B→A) increases" and the mechanism of the energy transfer responsible for them, some additional experiments were performed. In Figure 2 there are enhanced (a) and unenhanced (b) N_2 1pbs band emission spectra observed by mixing discharged N_2 with discharged O_2 streams in the flow reactor of reference [10]. These spectra show N_2 1pbs background emission intensity enhancements only – there are no 'red' singlet O_2 emissions in Figure 2. This indicates that the background emission increase observed in reference [2], is also due to N_2 1pbs emissions. The right-most spectrum of Figure 2 is running from 639.5 to about 618 nm (spectral region iii in Figure 2). The three N_2 1pbs emission bands shown in it, namely the 9,6 - 10,7 and 11,8 bands, manifest smaller increase in emission band intensity between the enhanced (case a) and the unenhanced (case b) band spectra than the corresponding increase in the 3,1 and 4,2 N_2 1pbs emission bands shown in the left-most spectrum (spectral region i in Figure 2).

Figure 3 also shows enhanced (a) and unenhanced (b) emission spectra of the N_2 1pbs, but at a lower total pressure, comparable to those in references 2-5.

Figure 3 shows the absence of "dimol" (a $^1\Delta$) O_2 emissions in the spectrum obtained by adding a stream of discharged O_2 into a flowing nitrogen afterglow generated by reacting undischarged N_2 in the flow reactor with Ar mw discharged in the side-arm of the apparatus described in reference 10. This technique of reacting undischarged N_2 with discharged Ar has been considered to lead to formation of N_2 (A $^3\Sigma_u^+$) practically free of N atoms [2-7,9]. Therefore, the experimental results in Figure 3 also support the involvement of N_2 (A $^3\Sigma_u^+$) with O_2 (a $^1\Delta g$) in the energy transfer reaction that leads to the reported "N_2 (B→A) increases".

Background emissions were also monitored in the same apparatus by adding discharged O_2 into flowing discharged gas mixtures of Ar with N_2. Neither these spectra, nor the previous ones, are corrected for non uniform spectral response of the grating and detector. They are shown in Figure 4. Figure 4 similarly shows enhanced (a) and
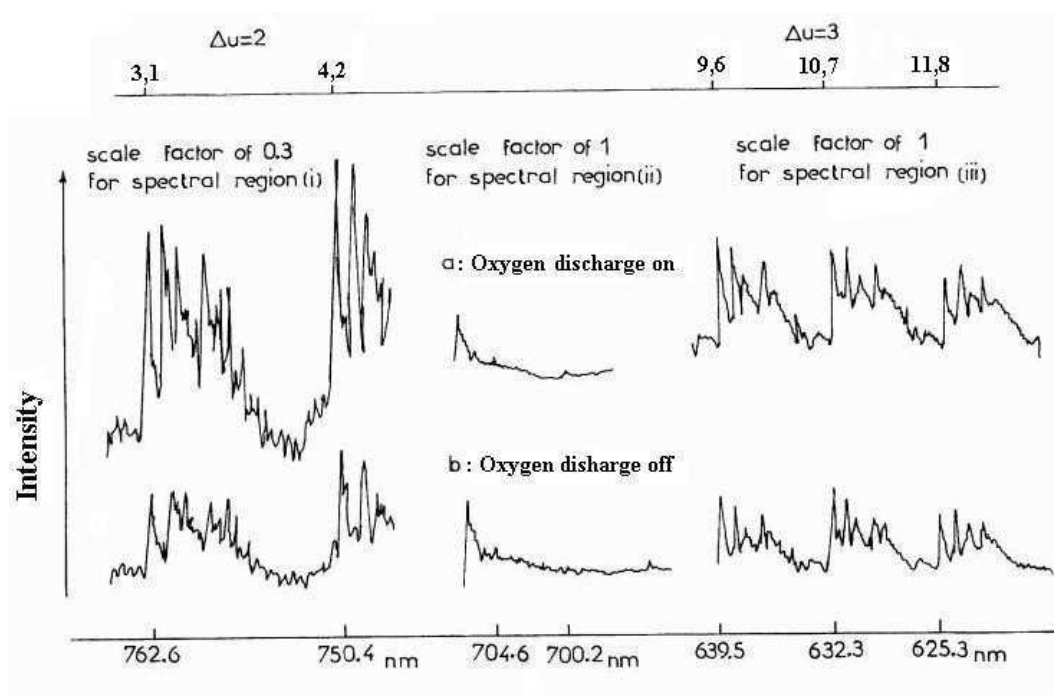
Fig. 2 N_2 (B $^3\Pi g \rightarrow$ A $^3\Sigma u^+$) emission spectra showing the $\Delta v=2$, and $\Delta v=3$ band sequences of the first positive band system (1pbs) , with and without discharged O_2. The vibrational levels of each band in a 1pbs N_2 (B $^3\Pi g \rightarrow$ A $^3\Sigma u^+$) sequence are shown over each band with the N_2 (B $^3\Pi g$) vibrational level of each band shown first. The spectra were obtained by adding (a, top spectra) discharged oxygen to a flowing nitrogen afterglow of discharged nitrogen, and (b, lower spectra) undischarged oxygen to the same nitrogen afterglow with the same scale factor. The three spectral regions (i), (ii) and (iii) extend on both sides of the peak wavelength for singlet molecular oxygen red and near_IR emissions: (i) the $\sim$761.8 nm for the O_2 (b $^1\Sigma g^+$) emission, (ii) the $\sim$703.2 nm for the 0,0 - 0,1 $2O_2$ (a $^1\Delta g$) emission, and (iii) the $\sim$633.4 nm for the 0,0 - 0,0 $2O_2$ (a $^1\Delta g$) emission. No such emissions are shown in these spectra. The top spectra in the spectral region (i) and (iii) show N_2 1pbs enhancement. In all cases $P_{N_2} = 15.6$ mbar and $P_{O_2} = 0.9$ mbar. The spectra are not corrected for grating and detector nonuniform spectral response.

unenhanced (b) emission spectra of the N_2 1pbs at a lower total pressure, comparable to those in references [2-5].

The experimental conditions used to obtain the spectra in both Figure 3 and Figure 4, were such as to lead to the appearance of an orange flame, visible to the naked eye. Flow rates used were between 3 and 10 bar cm^3/s. They corresponded to N_2^* flow times of $10-60$ ms to the observation ports of the 4.8 cm i.d. cylindrical flow reactor. The flame for Figure 3 was less bright than that for Figure 4, suggesting a lower concentration of N_2^* species responsible for the enhancements in the system of Figure 3 than in that of Figure 4. This is in agreement with reference [2], where six times more N_2 (A $^3\Sigma_u^+$) was reported when Ar + N_2 mixtures were discharged, also leading to N atom formation, than when reacting pure N_2 with discharged Ar, where extremely few N atoms were formed. As with Figures 2 and 3, Figure 4 also shows an absence of "dimol" ($^1\Delta$) O_2 emissions. As with Figure 2, both Figure 3 and Figure 4 show "N_2 (B$\rightarrow$A) increases". Figure 3 also shows that, addition of discharged oxygen into a flowing nitrogen afterglow generated by reacting undischarged N_2 in the flow reactor with Ar mw discharged, still produces
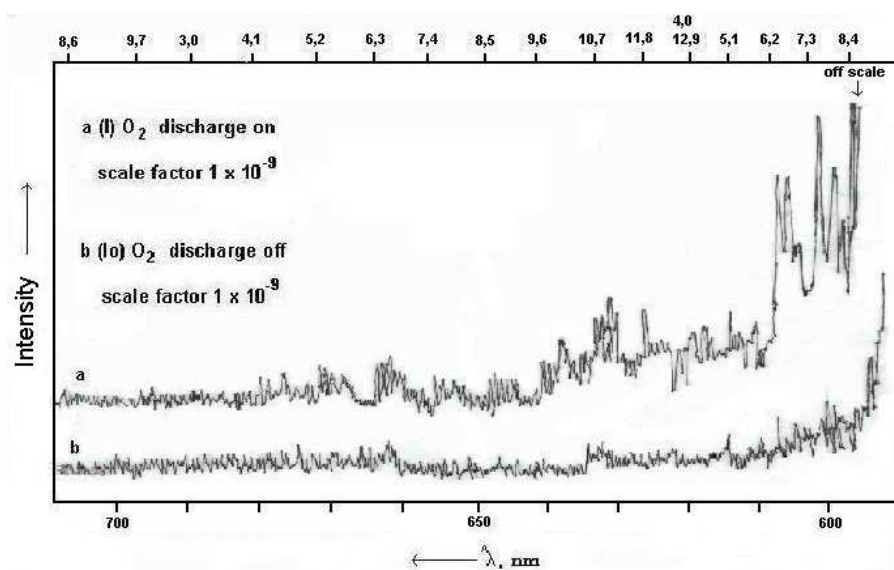
Fig. 3 N_2 (B $^3\Pi_g \rightarrow$ A $^3\Sigma_u^+$) emission spectra showing parts of the $\Delta v = 3$ and 4 band sequences of the first positive band system (1pbs), with and without discharged O_2. The vibrational levels of each band in a 1pbs {N_2 (B $^3\Pi$g $\rightarrow$ A $^3\Sigma$u$^+$)} sequence are shown over each band with the N_2 (B $^3\Pi$g) vibrational level of each band shown first. Active nitrogen was produced by reacting N_2 with discharged A_r. $P_{N_2} = 1.9$ mbar, $P_{A_r} = 1.3$ mbar and $P_{O_2} = 0.3$ mbar. The spectra are not corrected for grating and detector nonuniform spectral response.
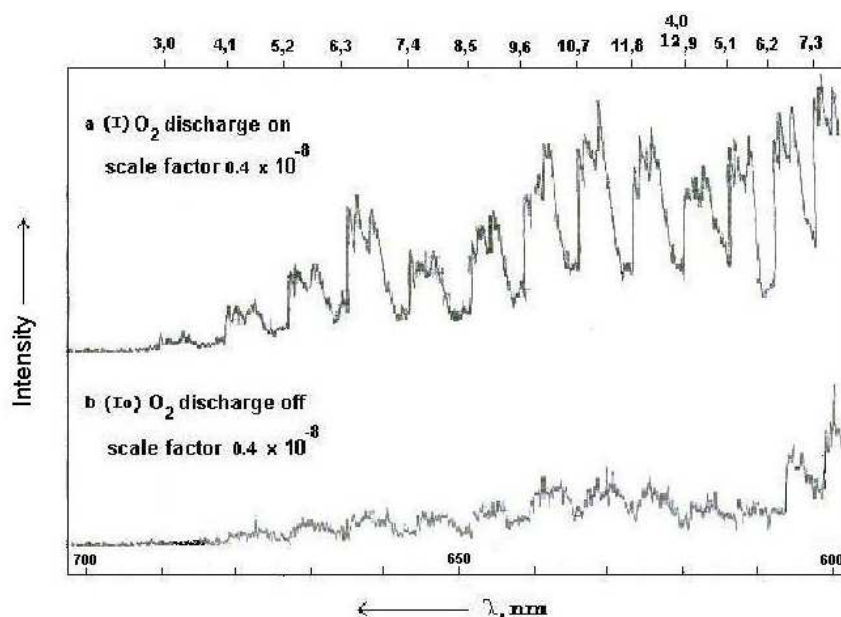

Fig. 4 N_2 (B $^3\Pi_g \rightarrow$ A $^3\Sigma_u^+$) emission spectra showing parts of the $\Delta v = 3$ and 4 band sequences of the first positive band system (1pbs) , with and without discharged O_2. The vibrational levels of each band in a 1pbs {N_2 (B $^3\Pi$g $\rightarrow$ A $^3\Sigma$u$^+$)} sequence are shown over each band with the N_2 (B $^3\Pi$g) vibrational level of each band shown first. Active nitrogen was produced by mw discharging a mixture of A_r and N_2. $P_{N_2} = 1.4$ mbar, $P_{A_r} = 0.3$ mbar and $P_{O_2} = 0.2$ mbar. The spectra are not corrected for grating and detector nonuniform spectral response.

nitrogen first positive band system emissions, even when the corresponding background (i.e., with the oxygen discharge off) nitrogen first positive band system emissions could

not be detected. This observation is in agreement with the reported similar previous observations [12,13,15] of "N_2 (B→A) increases" produced by adding discharged oxygen into a flowing nitrogen afterglow, where corresponding background emissions could not be detected. In these cases, though, the afterglow was generated by discharging pure nitrogen.

In the chemical system of Figure 3, N_2 (A $^3\Sigma_u^+$) has been considered [2-5,9] to be the only excited N_2 species present, with an almost complete absence of N atoms. This is further evidence for N_2 (A $^3\Sigma_u^+$) involvement in the energy transfer that leads to the orange flame. The occurrence of "N_2 (B→A) increases" [10-12] is further supported by the absence of "red" singlet ($^1\Sigma$) and "dimol" ($^1\Delta$) O_2 emissions in Figure 3, where "N_2 (B→A) increases" do appear. In reference [2], an additional technique was used to generate N_2 (A $^3\Sigma_u^+$) **without** N atoms by reacting N_2 with discharged (Ar + 0.1 % Xe) [2]. The application of this technique in reference [2] provides additional support for N_2 (A $^3\Sigma_u^+$) involvement in the aforementioned "N_2 (B→A) increases". The suggestion [13-14] that the mechanism of O(^{3}P) assisted **N atom** recombination might account for "N_2 (B→A) increases", is refuted by the observation of "N_2 (B→A) increases" even in the **absence** of N atoms (as argued in reference [2]). On the other hand, observation of "N_2 (B→A) increases" in the **absence** of N atoms is certainly in agreement with recent work [10-12] and the present proposal. Finally, there is further evidence [12] for N_2 (A $^3\Sigma_u^+$) involvement in: i). The long flow and interaction time of N_2* in this and in previous work [10-12], as well as in that of reference [2]. ii). The energy content of N_2*, and of Xe (^{3}P$_{0,2}$) used in reference [2]; and iii). The shorter lifetime of Xe (^{3}P$_0$) and of various N_2* species. For all of these reasons, the only N_2* species which appear energetically possible to be produced, and which, due to collisional and radiative lifetimes, survive long enough to participate in the expected "N_2 (B→A) increases" in the system of reference [2] are N_2 (A $^3\Sigma_u^+$) and N_2 (W $^3\Delta_u$, $v = 0$) [12]. Previous work with flow times longer than 60 ms to the observation ports used, as well as the present work with active nitrogen generated by reacting N_2 with Ar metastables –a technique considered [2-7,9] to generate a "clean" source of N_2 (A $^3\Sigma_u^+$)– supports N_2 (A $^3\Sigma_u^+$) involvement [10-12,15]. Similarly, in this and in previous work [10-12,15], the only possible molecular oxygen species responsible for the "N_2 (B→A) increases" appears to be O_2 (a $^1\Delta g$) because of its much longer collisional and radiative lifetimes.

The above data and analysis suggest that N_2 (A $^3\Sigma_u^+$, v) concentrations, henceforth [N_2 (A $^3\Sigma_u^+$, v)], are expected to be affected in all similar systems of nitrogen afterglows with discharged oxygen where the aforesaid "N_2 (B→A) increases" occur. Extraneous [N_2 (A $^3\Sigma_u^+$)] changes in experimental studies of N_2 (A $^3\Sigma_u^+$) decay by discharged O_2 can occur as the result of two factors. Firstly, because of N_2 (A $^3\Sigma_u^+$) interactions with O_2^*, which, as shown in this and previous work [10-12,15], come about in this phenomenon of N_2 1pbs emission enhancements. Secondly, because the observed "N_2 (B→A) increases" give rise to N_2 (A $^3\Sigma_u^+$) via cascade from N_2 (B $^3\Pi_g$). The extraneous change in [N_2 (A $^3\Sigma_u^+$, v)], because of "N_2 (B→A) increases", must be taken into account to correctly determine pertinent reaction rate constants. This extraneous change in [N_2 (A $^3\Sigma_u^+$, v)]

was not considered in a recent review [9].

The above analysis regarding the aforesaid extraneous [N_2 (A $^3\Sigma u^+$, v)] change in the studies of the {N_2 (A $^3\Sigma_u^+$,v) + O(^{3}P)} reaction is supported by an analogous redistribution of the initial vibrational excitation N_2 (A $^3\Sigma_u^+$) via cascade from vibrationally excited N_2 (B $^3\Pi_g$). Such a redistribution was invoked [18] in the excitation of N_2 (B $^3\Pi_g$, $v=1-12$) produced in the reaction of N_2 (A $^3\Sigma_u^+$) with N_2 (X $^1\Sigma_g^+$, v), in order to account for the discrepancy between the excitation rate coefficient of the product N_2 (B $^3\Pi_g$) (3×10^{-11} cm^3 molecule^{-1} s^{-1}) and the removal rate coefficient of the reactant N_2 (A $^3\Sigma_u^+$) (3.5×10^{-12} cm^3 molecule^{-1} s^{-1}). The N_2 (A $^3\Sigma_u^+$) vibrational redistribution via cascade from N_2 (B $^3\Pi_g$) can lead to lower {N_2 (A $^3\Sigma_u^+$, v) + O(^3P)} reaction apparent rate constants because of addition of N_2 (A $^3\Sigma_u^+$), whilst the N_2 (A $^3\Sigma_u^+$) interaction with O_2^* can lead to higher apparent rate constants because of "removal" of N_2 (A $^3\Sigma_u^+$). The N_2 (A $^3\Sigma_u^+$, v) "removal" may probably be apparent because of its further excitation, as indicated in interpretation of previous data in references [10-12 and 15]. N_2 (A $^3\Sigma_u^+$,v) excitation by fast reaction with O_2^* may lead to direct crossing into N_2 (B $^3\Pi_g$) collisionally, or it may lead to more highly excited N_2 (A $^3\Sigma_u^+$, $v'>v$), as shown in Figure 1. The maximum energy per collision that can be transferred is the potential energy content of O_2 (a $^1\Delta$g) above that of O_2 (X $^3\Sigma_g^-$, $v=0$). The energy difference between O_2 (a $^1\Delta g$, $v=0$) and O_2(X$^3\Sigma_g^-$,$v=0$) is 0.9787 eV or $\sim$7894 cm^{-1}, shown in Figure 1 in terms of the energy difference between the vibrational levels $v=7$ and $v=1$ of the N_2 (A $^3\Sigma_u^+$) state. Figure 1 shows some N_2 (A $^3\Sigma_u^+$, v'') vibrational levels very closely equienergetic with corresponding N_2 (B $^3\Pi_g$, v') levels. Consideration of available energy dictates that excitation to N_2 (B $^3\Pi_g$) due to of O_2 (a $^1\Delta$g) with N_2 (A $^3\Sigma_u^+$, v) may occur only for $v>0$, as Figure 1 shows.

The energy transfer that leads to the observed "N_2 (B→A) increases" should also be taken into account in (upper) atmospheric models (e.g., for low-altitude auroral afterglows, red sprites and dayglow) [19-20] or anywhere such N_2 (A $^3\Sigma_u^+$) interactions matter (e.g., in studies of discharges and plasmas) [1,2,8]. It should be noted that there may be additional redistribution of the initial N_2 (B $^3\Pi_g$, v) excitation by energetic electrons in the upper atmosphere, caused by this non-uniform homogeneous molecular collisional energy transfer. N_2 (B $^3\Pi_g$, v) excitation redistribution may particularly take place in auroral arcs extended to lower altitudes in the atmosphere because of increased energies of the primary exciting electrons, where molecular collisions are also sufficiently frequent. This potential additional redistribution may result in a visible difference in the emitted radiation from low-altitude auroras below the critical altitude of $\sim$100 km for molecular collisional energy transfer to occur [19-20]. It may not be easy to distinguish this additional redistribution from the redistribution caused by ground state molecules [10,19], like N_2 and O_2, in the low-altitude auroral afterglow [19-20], unless it is combined with additional observations.

An estimate of the reaction rate constant for collisional electronic energy transfer from O_2 (a $^1\Delta g$) to N_2 (A $^3\Sigma_u^+$, v), k_{aA} may be obtained by reinterpreting previous data. Such data includes the decrease of the concentration of either O_2 (a $^1\Delta g$) or N_2 (A $^3\Sigma_u^+$) in a

flowing nitrogen afterglow. The first set of data is obtained from studies of the reaction $\{O_2 \ (a \ ^1\Delta g) + (\text{discharged } N_2)\}$, ascribed to reaction of $O_2 \ (a \ ^1\Delta g)$ with N atoms, as shown in reference [21], and as explicitly acknowledged in reference [17]. Although the assumption about $O_2 \ (a \ ^1\Delta g)$ reacting with N atoms appears to be in conflict with the conclusion of reference 22, i.e., that N atoms do not react with $O_2 \ (a \ ^1\Delta g)$ –since the monitored N atom concentration was observed not to decay–, both observations are shown below to be reconciled. The second set of data is obtained from studies of the reaction $\{N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon) + (\text{discharged } O_2)\}$, ascribed to reaction of $N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon)$ with $O(^3P)$ atoms [1-9]. It is of interest that the (low) concentration of $O_2 \ (a \ ^1\Delta g)$ used is reported to be proportional to that of $O(^3P)$ atoms in some experiments [15] in a nitrogen afterglow with oxygen in reference [11], and on page 2374 in reference [3], under the experimental conditions of the study of the AO reaction. Hence, the correlation between $N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon)$ and $O(^3P)$, under pseudo-unimolecular conditions, is the same as that between $N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon)$ and $O_2 \ (a \ ^1\Delta g)$. No assumption of proportionality between $[O(^3P)]$ and $[O_2 \ (a \ ^1\Delta g)]$ is used in any way in the calculations below. The proportionality is just pointed out to account for the agreement among previous results by others, as in the case of the assumed reaction $\{O_2 \ (a \ ^1\Delta g) + N\}$.

The $N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon)$ versus $O(^3P)$ experimental data in the AO reactions may be also employed for the study of the $N_2 \ (A \ ^3\Sigma_u^+, \ \upsilon)$ (apparent) decay contributed by $O_2 \ (a \ ^1\Delta g)$ in the energy transfer reaction aA. It should be noted that the $O_2 \ (a \ ^1\Delta g)$ decay (measured photometrically [11,15], by photonionization [21], and mass-spectrometrically [17]) in a nitrogen afterglow generated by mw discharged nitrogen remains the **same**, regardless of the presence or absence of $O(^3P)$ [15,17]. Hence $N_2 \ (A \ ^3\Sigma_u^+)$ reacts with $O_2 \ (a \ ^1\Delta g)$ to a greater extent than with $O(^3P)$ in the reaction $\{N_2 \ (A \ ^3\Sigma_u^+) + (\text{discharged } O_2)\}$. If that were not the case, the observed $O_2 \ (a \ ^1\Delta g)$ decay, assigned to reaction with $N_2 \ (A \ ^3\Sigma_u^+)$ in this work, would depend on the $[O(^3P)]$, which is contrary to the experimental observations [15,17].

An observed decrease in the $O_2 \ (a \ ^1\Delta g)$ concentration is the only indisputable experimental observation of a reactant in the studies reported in references 17 and 21. The $[O_2 \ (a \ ^1\Delta g)]$ decay was assigned to N atoms in the $\{O_2 \ (a \ ^1\Delta g) + (\text{discharged } N_2)\}$ reaction. Equally tentative and questionable is the claim in reference [21] that NO is formed in the $O_2 \ (a \ ^1\Delta g) + N \rightarrow NO + O$ reaction. There is no product formation evidence, because of experimental inability to detect such reaction products. In fact reference [21] reported that the experimental technique used did not permit their detection. The proportionality between the $O(^3P)$ and $O_2 \ (a \ ^1\Delta g)$ concentrations, invoked in this analysis, is analogous to the proportionality between the N and excited N_2 concentrations, invoked in reference [17] to rather discount the possibility that the assumed reaction $O_2 \ (a \ ^1\Delta g) + N(^4 S) \rightarrow NO + O(^3P)$ occurs, because of the observed [10,15,17] initial "$N_2 \ (B \rightarrow A)$ increases". In contrast, this work does not arbitrarily assume reaction aA, but deduces from the present and previous [10-12,15] experimental observations that such a reaction does take place. Reaction aA can be inferred because both reactants are present in the system, both have been shown to be involved in energy transfer in discharged N_2 –with or without Ar- and

O_2, and both their concentrations are decreased, as references [1-8,10,11,15] and [17,21] show. In fact the inclusion of reaction aA unifies all past observations, even including the $\{O_2 \ (a \ ^1\Delta g) + (discharged \ N_2)\}$ reaction reported [17,21,22]: In addition, reference [22] demonstrated that there was no N atom involvement in the reaction aN, which directly conflicts with the conclusion of references [17,21], which attributed the observed O_2 (a $^1\Delta g$) decay to reaction with N atoms. However all of the experimental evidence in references [17,21,22] regarding the reactants of the $\{O_2 \ (a \ ^1\Delta g) + (discharged \ N_2)\}$ reaction can be reconciled by the inclusion of the aA reaction. Both the O_2 (a $^1\Delta g$) decay reported in references [17,21] and the lack of significant N atom reactive involvement reported in reference [22] are supported by the reaction aA deduced in this work. The apparently conflicting evidence on the $\{O_2 \ (a \ ^1\Delta g) + (discharged \ N_2)\}$ reaction actually studied in references [17,21] arose because reaction aA was not considered. Hence, both references [17] and [21] correctly reported the O_2 (a $^1\Delta g$) decay in (discharged N_2). Reference [22] correctly reported no N atom involvement in the reaction aN, since the O_2 (a $^1\Delta g$) decay observed appears to be due not to its reaction with N atoms, but rather to transfer of its energy to N_2 (A $^3\Sigma_u^+$) species in the discharged N_2, in accordance with the evidence reported in this work.

For the determination of a chemical reaction rate constant, k, in a flow reactor, the mean flow velocity, u, and the reaction (contact) time t = z/u, after the mixing of the two reactants, are also employed, where z is the reaction distance from the mixing region of the reactants. A value of k is obtained [2-4] either by varying the concentration of a reactant, C, which is a function of the concentration of the second reactant Q, from

$$k = \frac{u}{z} \frac{d\ln\left(\frac{C_o}{C}\right)}{dQ}, \tag{1}$$

or from the variation of C with the reaction distance at **constant** Q, (the second reactant being in abundance or at a steady state), from

$$k = \frac{u}{Q} \frac{d\ln\left(\frac{C_o}{C}\right)}{dz}. \tag{2}$$

C_o represents C at t=0, i.e. the initial reactant concentration. It will now be shown, in the light of the present and previous evidence [10-12] and the reinterpretation of previous data on the aN and AO reactions, that k_{aA} is at least on the order of 10^{-10} molecule^{-1} cm^3 s^{-1}, if not gas kinetic or even larger. The analysis draws on (i) O_2 (a $^1\Delta g$) depletion data in Figures 2 and 6 in reference [21] and in Table 1 of reference [17],(ii) N_2 (A $^3\Sigma_u^+$) concentration data [8,23,24] and (iii) N_2 (A $^3\Sigma_u^+$) depletion data and oxygen concentrations data in references [2-4,9]. Datasets (i) and (ii) are employed in the determination of C=[O_2 (a $^1\Delta g$)] and Q = [N_2 (A $^3\Sigma_u^+$)]; Datasets (iii) can be employed in the determination of C=[N_2 (A $^3\Sigma_u^+$)] and Q=[O_2 (a $^1\Delta g$)] for additional estimation of k_{aA}.

The estimation of k_{aA} proceeds as follows:

(i) Most of the O_2 (a $^1\Delta g$) quenching in reference 17, if not all, is ascribed to N_2 (A $^3\Sigma_u^+$) species (in reaction aA) instead of N atoms. Consequently this assignment

results in the substitution of $[N_2 \ (A \ ^3\Sigma_u^+)]$ for $[N]$ in the above equations used in previous analyses;

(ii) The value $k=1.7 \times 10^{-15}$ molecule^{-1} cm^3 s^{-1}, obtained from Table 1 of ref. [17] for the reaction aN, is used in equation (5) below; and

(iii) A value of $\sim 5 \times 10^9$ molecules cm^{-3} for $[N_2 \ (A \ ^3\Sigma_u^+)]$ [8] is used, instead of 1.3×10^{-2} Torr $\sim 4.6 \times 10^{14}$ atoms cm^{-3} for Q = $[N]$ at 300 K (in the observation region sufficiently far away from the discharges in references 17,21]) that appears in Table 1 of reference [17].

To obtain an estimate of k_{aA} using equation (2):

$$k_{aA} = \frac{u}{[N_2(A^3\Sigma_u^+)]} \frac{\mathrm{dln}\frac{[O_2(a^1\Delta g)]_o}{[O_2(a^1\Delta g)]}}{\mathrm{d}z}, \tag{3}$$

or

$$k_{aA} = \frac{u}{[N]} \frac{\mathrm{dln}\frac{[O_2(a^1\Delta g)]_o}{[O_2(a^1\Delta g)]}}{\mathrm{d}z} \frac{[N]}{[N_2(A^3\Sigma_u^+)]}, \tag{4}$$

or

$$k_{aA} = k \frac{[N]}{[N_2(A^3\Sigma_u^+)]}. \tag{5}$$

After numerical substitution, a value for k_{aA} is obtained,

$$k_{aA} = 1.7 \times 10^{-15} \cdot (4.6 \times 10^{14}/\sim 5 \times 10^9) = 1.6 \times 10^{-10} \text{ molecule}^{-1}\text{cm}^3\text{s}^{-1}.$$

In addition, use of the value of $[N_2 \ (A \ ^3\Sigma_u^+)] = 2.4 \times 10^9$ in the low $N_2 + O_2$ pressure product channel study [24] that reported N_2 and O_2 partial pressures comparable to those in reference [17] leads to

$$k_{aA} = 1.7 \times 10^{-15} \cdot (4.6 \times 10^{14}/2.4 \times 10^9) = 3.3 \times 10^{-10} \text{ molecule}^{-1}\text{cm}^3\text{s}^{-1}.$$

Substantially higher values of chemical reaction rate constants, even exceeding 10^{-9} molecule^{-1} cm^3 s^{-1} were suggested for $N_2 \ (A \ ^3\Sigma_u^+, v)$ reactions cited in reference [23].

4 Further discussion and conclusion

The above large rate constant estimates, supported by independent data from different relevant experiments, strongly suggest that transfer of energy from $O_2 \ (a \ ^1\Delta g)$ to N_2 $(A \ ^3\Sigma_u^+)$ does take place, in contrast to the $N_2 \ (A \ ^3\Sigma_u^+)$ energy transfer to $O_2 \ (a \ ^1\Delta g)$ speculatively suggested in references [2-4,9]. An alternative hypothesis of energy transfer between $N_2 \ (a^{'} \ ^1\Sigma_u^-)$, or another N_2^* state, and $O_2 \ (a \ ^1\Delta g)$ in the above analysis for the active nitrogen systems of references [17] and [21] could not succeed: it would lead to a rate constant estimate that has no physical meaning. The remaining **traces** of N_2 $(a^{'} \ ^1\Sigma_u^-)$ [25] and of other N_2^* states (with concentrations of orders of magnitude lower than that of $N_2 \ (A \ ^3\Sigma_u^+)$ in the denominator of eq. (5)), after reaction times of tens of ms at the sampling ports, would lead to unacceptably high values for the rate constant.

Moreover, the observations for the "clean" source of N_2 (A $^3\Sigma_u^+$) used in the present work and [12] in reference [2], and various other considerations for quenching effects [15], make the involvement of any other N_2^* or $N_2^\clubsuit$ state (in energy transfer with O_2 (a $^1\Delta g$) that can lead to the "N_2 (B→A) increases" [10-12], when discharged oxygen is added) even more unlikely. Thus, it is clear that the (fast) involvement of N_2 (A $^3\Sigma_u^+$) and O_2 (a $^1\Delta g$), invoked in this work in the way shown in Figure 1, must certainly occur in the "N_2 (B→A) increases". The reaction aA provides a well justified, unifying, and novel interpretation of the experimentally observed decays in active nitrogen and oxygen of the metastable species O_2 (a $^1\Delta g$) and N_2 (A $^3\Sigma_u^+$). The existing interpretations fail: The assumed reactive involvement of N atoms [17,21] (albeit slow, if it actually occurs) is in conflict with the lack of N atom involvement reported in reference [22], in the study of the $\{O_2$ (a $^1\Delta g$) + (discharged N_2)$\}$ reaction [17,21,22,26]. A second existing interpretation is the fast involvement of $O(^3P)$ atoms in the $\{N_2$ (A $^3\Sigma_u^+$, υ) + $O(^3P)\}$ reactions, which appear to be affected by the "N_2 (B→A) increases", so as to need reassessment. The present interpretation is the involvement of O_2 (a $^1\Delta g$) and N_2 (A $^3\Sigma_u^+$), deduced by eliminating other possible oxygen and nitrogen species in accounting for the observations in this and in previous work [10-12]. Because one oxygen and, at least, one nitrogen species have to be involved in the energy transfer that leads to an orange flame as a result of "N_2 (B→A) increases" in a flowing afterglow of active nitrogen [10-12], when discharged oxygen is added to it, and because all other oxygen and nitrogen species have been eliminated, only O_2 (a $^1\Delta g$) and N_2 (A $^3\Sigma_u^+$) are left to be responsible for the observed energy transfer.

In conclusion, this work does not assume, but it clearly deduces from experiments -performed by this author, and by others-, that the reaction aA clearly appears to take place. The occurrence of reaction aA reconciles even old observations [2,5,13,14,17,21, 22,26,27]. It is important that

(i) both reactants in reaction aA are present and are involved in energy transfer in discharged N_2 -with or without Ar- and O_2 that even leads to the reported orange flame.

(ii) The concentrations of both of these species have been shown to decrease in active nitrogen and oxygen [1-8,11,15,28 and 17,21], and

(iii) The concentrations of O_2 (a $^1\Delta g$) and $O(^3P)$, used, are proportional [3,11,15]; therefore the correlation reported [1-9] between N_2 (A $^3\Sigma_u^+$) and $O(^3P)$ also holds between N_2 (A $^3\Sigma_u^+$) and O_2 (a $^1\Delta g$). In addition, a consistent, reasonable estimate for the pertinent rate constant is deduced (at least on the order of 10^{-10} molecule^{-1} cm^3 s^{-1}) by using two different approximations. Such agreement is not likely to be fortuitous. Future work will provide further evidence about the mechanism of this intriguing, elusive energy transfer that leads to the orange flame, and that affects several research areas.

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