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ENERGY TRANSFERS IN N_2-O_2 PLASMAS: RECOGNIZING AND MEASURING ACTIVE SPECIES

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General

Energy transfers in N_2-O_2 plasma touch numerous topics of kinetics modeling, diagnostics and applications of partially ionized N_2-O_2 admixtures [1-8]. Apart from electrons and ions, in N_2-O_2 plasmas the most relevant atomic and molecular active species are [1]: metastable species $O(^1D)$, $O(^1S)$, $N(^2D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, $N_2(A^3\Sigma_u^+)$, and $N_2(a'^1\Sigma_u^-)$, and neutral ground state $N_2(X^1\Sigma_g^+,v)$, $O(^3P)$, $N(^4S)$. Recognizing enenrgy transfers by such species has been the issue of numerous investigations in laboratory plasma sources both at low (tens of milliTorr) and high (atmospheric) pressure, looking at plasma chemistry studies related to environmental [2], sterilization [3], material processing [4], flow control [5], as well as at natural atmospheric discharges occurring in the upper atmosphere at high altitude like transient luminous events (sprites, elves, blue jets, …) [6]. Energy transfers by excited N_2-O_2 mixture and byproducts have been seen to be important in gas phase and gas-surface reactivity around space vehicles during re-entry in the Earth atmosphere [7]. Then plasma jets source have been used in laboratory to generate flows of active species by nozzle expansion [8]. Actually various papers review elementary kinetics in N_2, O_2 and N_2-O_2 admixtures [9-11] under various low temperature plasma conditions all focusing on non equilibrium nature as the most relevant aspect both at low and high pressure. The state-to-state nature of non-equilibrium elementary kinetics introduces a significant complexity in the modeling of plasma reactivity [12], also considering that in most cases the presence of plasma surface interaction introduce further reaction channels by gas-surface processes [1].

Recognizing energy transfers and active species helps much the investigations of both laboratory and atmospheric non-equilibrium plasmas. Any energy transfer, in fact, brings memory not only of the state to-state cross section of the elementary process but also of the density and state distribution of active species involved in the collision process. Recognizing/measuring excitation/density of various active species (electrons, vibrational excited molecules, atomic and molecular nitrogen/oxygen metastables) and byproducts in N_2-O_2 plasma sources does require several diagnostics tools and often their limits restrict the direct experimental evidence to only some most significant species. On the other hand often understanding the properties of plasma does require investigations of plasma transitions from space region or time domain at high electric field and/or electron density to one at much lower (null) values, i.e. transition *glow - afterglow* or *discharge –post-discharge.* Dynamics of reactive system depends on time scale of various energy transfers that spans from microseconds to tens-hundreds of milliseconds at pressure around Torr,

while from few nanosecond to few milliseconds at atmospheric pressure. Fast time scale processes are mainly dominated by electron processes while long time scale by energy transfer by long lived species like vibrational excited molecule and metastable. This issue is receiving large attention in partially ionized N_2, O_2 and N_2-O_2 admixtures plasmas at low [9, 14, 15] and high pressure [16-18]. Particular are streamer based discharges, corona at high pressure and sprites at low pressure [6] and dielectric barrier discharge (DBD) that are characterized by pulsed/traveling ionization wave forming largely inhomogeneous plasmas both in time and space. Space/time randomly filamentary microdischarges of tens-hundreds of micron plasmas characterize air like atmospheric pressure DBDs. Diagnostics of energy transfers in such sources is a challenge [17-24], with respect to low/high pressure glow sources for which various technique with adequate space/ time resolution (laser spectroscopy, mass-spectrometry, Langmuir probes) have been applied successfully.

This lecture will focus on our recent studies in recognizing and measuring some active species involved in energy transfer in N_2-O_2 admixture in various plasma sources at low and atmospheric pressure. Low pressure capacitive (CCP) / inductive (ICP) coupling RF plasma reactors driven under modulated regime and supersonic plasma jets will be considered, and atmospheric pressure a.c. current dielectric barriers discharge (DBD), both volume and surface configuration, driven under continuous /modulated regime as well. Moving from low to high pressure and from glow to afterglow space/time regimes conditions, the outcomes of $N_2(X^1\Sigma_g^+,v)$, $N_2(A^3\Sigma_u^+)$, $N(^4S)$, $O(^3P)$, $N_2(C^3\Pi_u)$, $N_2(B^3\Pi_g)$, $N_2^+(B^2\Sigma_u)$, $NO(X^2\Pi)$, $NO(A^2\Sigma)$ and their evolution in various plasma sources will be examined highlighting various spectroscopic methodologies based on laser or on plasma emission recently used for measuring active species and recognizing excitation, relaxation and quenching energy transfers.

The following energy transfer related issues will be focused:

1**) Time evolution of $N_2(X^1\Sigma_g^+, v)$ molecules and $N(^4S)$ in N_2 ICP discharge.** The excitation/relaxation of $N_2(X^1\Sigma_g^+, v\leq 4)$ molecules measured in ICP 13.6 MHz discharge, driven by a planar antenna under ON-OFF modulation, is focused. Measurements are carried out at 2 Torr by folded box-CARS [25, 26]. The rising of first level temperature to a high value (about 7000 K), during the discharge ON- time (5 ms) and the quite slow relaxation during discharge OFF–time (15 ms) occurs in presence of rising of $N(^4S)$ monitored by TALIF. At lower pressure, because of low pressure limits of CARS, $N_2(X^1\Sigma_g^+, v)$ excitation is inferred from the excitation/relaxation of $N_2(C^3\Pi_u,v)$ through a collisional-radiative analysis based on state-to-state electron and $N_2(A^3\Sigma_u^+)$ metastable processes. A significantly higher vibrational excitation of $N_2(X^1\Sigma_g^+, v\leq 4)$ characterizes the lower (0.2 Torr) pressure case. Highlights on the discharge H-E modes regime at low and high pressure are achieved by time resolved $N_2(C^3\Pi_u)$ emission in RF cycle [26] and by electron data by time resolved Langmuir probe in [27]. Highlights on $N_2(A^3\Sigma_u^+,v)$ metastable are achieved form literature dealing with its direct measurement in N_2 ICP H-mode discharge [28] and in N_2-O_2 admixtures in capacitive coupled RF discharge [29].

2) Space/time evolution of N, O, NO and electronic excited state excitation in N_2, N_2-O_2 supersonic non-equilibrium plasma jet. Highlights on measured axial/radial expansion structures of $NO(X^2\Pi)$, $N(^4S)$, $O(^3P)$ ground state species monitored by one /two photon LIF and N_2-SPS and NO-gamma band emission from $N_2(C^3\Pi_u)$, $NO(A^2\Sigma)$ electronic states address the energy transfer competition between electrons, $N_2(A^3\Sigma_u^+)$ metastable as well as N+O

recombination in a supersonic low pressure non-equilibrium plasma jet in N_2 and N_2-O_2 air like mixture. Ground state atomic and molecular species as well as excited $N_2(C^3\Pi_u)$ state and NO $(A^2\Sigma)$, evidence with a different degree of modulation the expansion- compression waves typical of over-expanded and slightly under-expanded free jet generated with supersonic nozzle [8, 30, 31]. The analysis of the vibrational distribution of $(C^3\Pi_u)$ state at various distance from nozzle exit highlights RF plasma jet as a space afterglow helped by a weak electric field and modulated by fluid-dynamics structures (expansion - compression waves). In N_2 plume even at long distance from nozzle, i.e. at estimated averaged time of few millisecond, electrons and $N_2(A^3\Sigma_u)$ are competing in the excitation of N_2 electronic states. In N_2-O_2 plume, instead, excitation processes are by electron impact being $N_2(A^3\Sigma_u)$ a minor specie because of quenching by N, O, and O_2. $NO(A^2\Sigma)$ excitation highlights energy transfer by $N_2(A^3\Sigma_u)$ and/or by N+O+M recombination.

3) Time evolution of $N_2(A^3\Sigma_u^+)$, in N_2-O_2 admixture in volume and surface dielectric barrier discharge at atmospheric pressure. The difficult detection of $N_2(A^3\Sigma_u)$ at atmospheric pressure has intrigued the analysis of space and time afterglows of filamentary/glow discharge regime of DBD. Its measurement at low pressure is rather straightforward [29], but at high pressure has been a challenge for long time. Recently $N_2(A)$ has been measured by Optical-Optical Double resonance Laser induced fluorescence (OODR-LIF) in volume [17] and surface DBDs [18, 19]. Actually also standard single photon LIF has been successful applied [20] for measuring $N_2(A)$ in streamer generated by point-plane atmospheric pressure corona in N_2/O_2 admixtures. In both cases LIF calibration was obtained using features of $N_2(A)$ metastable energy transfers. Very recently also CRDS has been applied to measure $N_2(A)$ time evolution in pulsed nanosecond pin-to-pin repetitive atmospheric pressure glow discharge in N_2-O_2 admixture [23]. Here we highlight the effect of small addition of O_2, and NO to N_2 in modulated both volume and surface DBDs. and the behavior of $N_2(A)$ in discharge, post-discharge and space afterglow.

4) About quenching of N_2 $(C^3\Pi_u, v)$ and $N_2^+(B^2\Sigma_u v)$ by N_2 and O_2 data sets

Monitoring of plasma parameters and kinetic processes by OES from electronic excited state of nitrogen is a frequent task in atmospheric pressure plasma source being emission very often the most accessible and easy tool to look at the discharge processes. However, use of OES does require not only a preventive study to ascertain the excitation mechanisms that produce the monitored emissions but also a knowledge of quenching affecting the emitting states. Recently the large difference in the quenching data set available for N_2 $(C^3\Pi_u, v)$ and $N_2^+(B^2\Sigma_u v)$ by N_2 and O_2 is calling the attention of users [24]. Data set seem to be affected by different methodologies employed for preparing these excited states. Essentially selective laser prepared states give quenching rates by N_2 higher than non selective ones based on discharge excitation. Differences are minor in the case of quenching by O_2. In this context we highlight the vibrational relaxation in N_2 $(C^3\Pi_u, v)$ manifold [32] and other possible drawbacks, likely surviving post-discharge excitation/relaxation energy transfers, affecting non selective state-prepared quenching measurements of N_2 $(C^3\Pi_u, v)$ and $N_2^+(B^2\Sigma_u,^+, v)$.

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