$O_2(^1\Delta)$ AND $I(^2P_{1/2})$ PRODUCTION IN FLOWING AFTERGLOWS FOR OXYGEN-IODINE LASER: EFFECT OF NO/NO_2 ADDITIVES*

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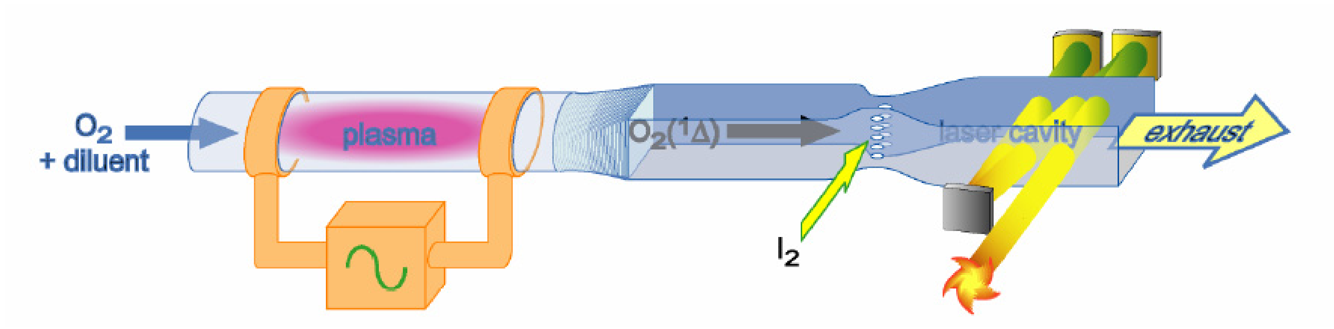
AGENDA

- Oxygen-Iodine Lasers: Why use electrical discharges?
- Description of models *nonPDPSIM* (2d), *GlobalKIN* (plug-flow).
- Oxygen-Iodine reaction kinetics with I_2 injection and NO_x additives.
- Scaling with power and NO mole fraction in the discharge.
- Effect of NO_2 addition in the afterglow.
- Concluding Remarks.

OXYGEN-IODINE LASERS: eCOILS

- **In chemical oxygen-iodine lasers (COILs), oscillation at 1.315 µm $[I^{2(}P_{1/2}) \rightarrow I(^2P_{3/2})]$ in atomic iodine is produced by collisional excitation transfer from $O_2(^1\Delta)$ to I_2 and I.**
- **Supersonic expansion required for gain to reduce importance of back-reaction.**
- **First generation COILs use liquid phase reactions to generate $O_2(^1\Delta)$ from a basic solution of H_2O_2 with Cl_2.**
- **In electrically excited COILs, a plasma is used to generate the $O_2(^1\Delta)$ by electron impact excitation of O_2.**



eCOILS: EFFECT OF NO/NO_2

- Electron impact excitation of O_2 has three primary branches:

$$e + O_2 \rightarrow O + O + e$$
$$\rightarrow O_2(^1\Delta, {}^1\Sigma) + e$$

- O atom production has advantages and disadvantage:

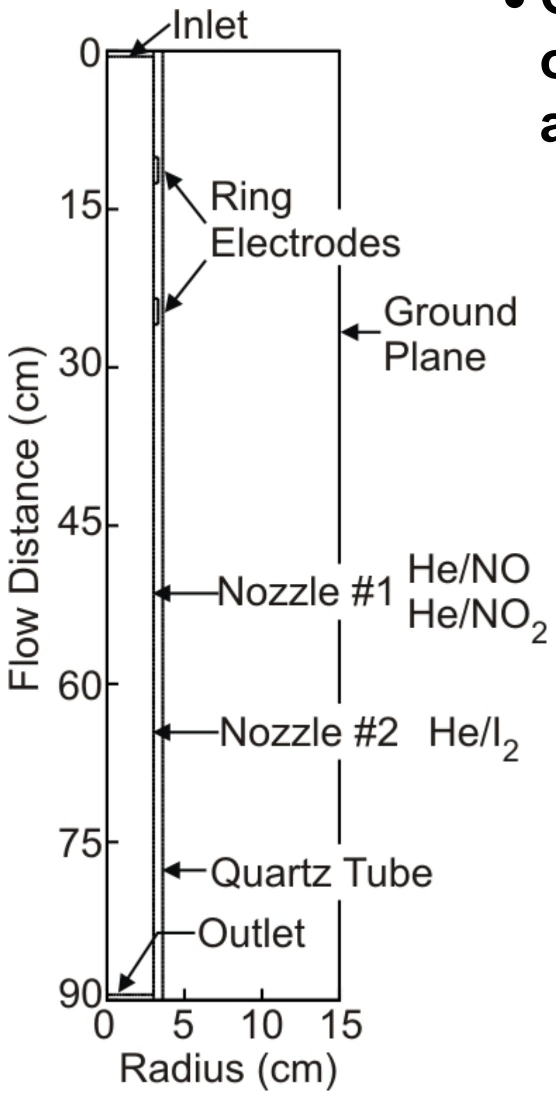
$$O + I_2 \rightarrow IO + I$$
$$O + IO \rightarrow O_2 + I$$
$$O + I^* \rightarrow O + I$$

- NO and NO_2 additives control densities of O atoms.

$$NO_2 + O \rightarrow NO + O_2 \;\; (k = 4.2\times10^{-12}\ cm^3\ s^{-1}) \;\; (FAST)$$
$$NO + O + M \rightarrow NO_2 + M \;\; (k = 1.0\times10^{-31}\ cm^6\ s^{-1}) \;\; (SLOWER)$$

- NO: Reduce T_e to optimal values (1 - 1.5 eV).

GEOMETRY AND SCOPE



- **Computationally investigate consequences of NO and NO$_2$ additives on O$_2$($^1\Delta$) production and gain.**
  - **Inlet: 3 Torr, 6 slpm, He/O$_2$/NO: 70-x/30/x.**
  - **Power deposition: 40 – 400 W.**
  - **1st nozzle: 36 sccm He/NO or He/NO$_2$.**
  - **2nd nozzle: 100 sccm He/I$_2$.**
  - **Yield of O$_2$($^1\Delta$) and gain (G).**

$$Y = \frac{[\mathrm{O_2}(^1\Delta)] + [\mathrm{O_2}(^1\Sigma)]}{([\mathrm{O_2}] + [\mathrm{O_2}(v)] + [\mathrm{O_2}(^1\Delta)] + [\mathrm{O_2}(^1\Sigma)] + 0.5[\mathrm{O}] + 1.5[\mathrm{O_3}])}$$

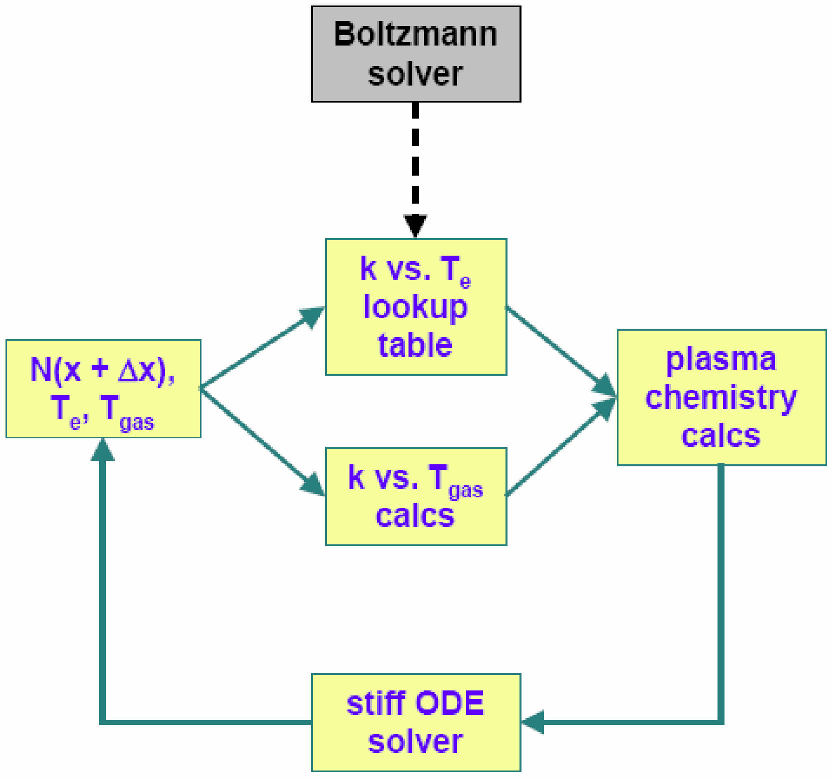
$$\mathrm{Gain} = \sigma([\mathrm{I}^*] - 0.5[\mathrm{I}]) \qquad \sigma = \left(1.33\times10^{-16}\right)\sqrt{\frac{1}{T_g}}\ \mathrm{cm}^2$$

DESCRIPTION OF 2-D MODEL

- **Node-centric finite volume method.**
- **Poisson's Equation for Electric Potential (including surface and volumetric charges).**
- **Continuity (electron, heavy particle collisions, surface chemistry, secondary emission), SG fluxes with advective flow field.**
- **Rates: Coefficients obtained from Boltzmann's equation solution for EED.**
- **Fluid: Density (ρ), Momentum (ρu, ρv) and gas temperature obtained using unsteady, compressible Navier-Stokes equations.**
- **Individual species advected with superimposed diffusive transport.**
- **Time integration by iterative Newton method using numerically calculated Jacobians.**

GLOBAL PLASMA MODEL

- Global model run in plug-flow mode.
- Boltzmann solver updates e-impact rate coefficients.
- Inputs:
  - Power density vs position
  - Reaction mechanism
  - Inlet speed (adjusted downstream for T_{gas})
- Assume no axial diffusion.



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$O_2 - I_2$ KINETICS: IMPORTANT REACTIONS

Iodine Dissociation:

$O_2(^1\Delta) + I_2 \rightarrow O_2 + I_2^*$ $(k = 7.0 \times 10^{-15}\ cm^{-3}\ s^{-1})$

$O_2(^1\Delta) + I_2^* \rightarrow O_2 + I + I$ $(k = 3.0 \times 10^{-15}\ cm^{-3}\ s^{-1})$

$O_2(^1\Sigma) + I_2 \rightarrow O_2 + I + I$ $(k = 2.8 \times 10^{-11}\ cm^{-3}\ s^{-1})$

$O + I_2 \rightarrow IO + I$ $(k = 1.4 \times 10^{-10}\ cm^{-3}\ s^{-1})$

$O + IO \rightarrow O_2 + I$ $(k = 1.4 \times 10^{-10}\ cm^{-3}\ s^{-1})$

Pumping Reaction:

$O_2(^1\Delta) + I \rightarrow O_2 + I^*$ $(k = 7.7 \times 10^{-11}\ (T_g/300)^{-1}\ cm^{-3}\ s^{-1})$

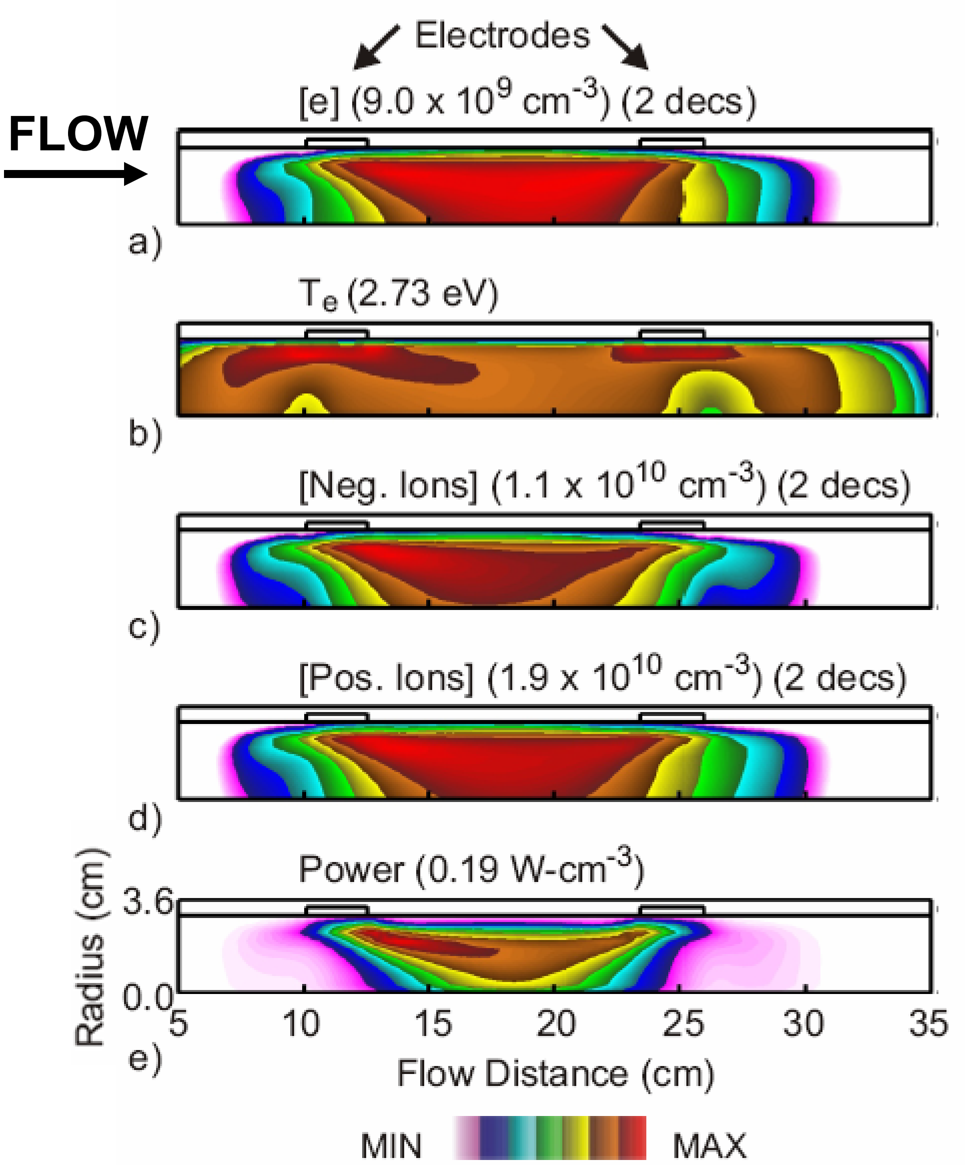
Quenching:

$O + I^* \rightarrow O + I$ $(k = 8.0 \times 10^{-12}\ cm^{-3}\ s^{-1})$

$O_2 + I^* \rightarrow O_2(^1\Delta) + I$ $(k = 1.0 \times 10^{-10}\ (T_g/300)^{-1}\ e^{-403/Tg}\ cm^{-3}\ s^{-1})$

- Ref: A. D. Palla Proc. SPIE. Vol 6101, 610125 (2006).

BASE CASE: PLASMA CHARACTERISTICS

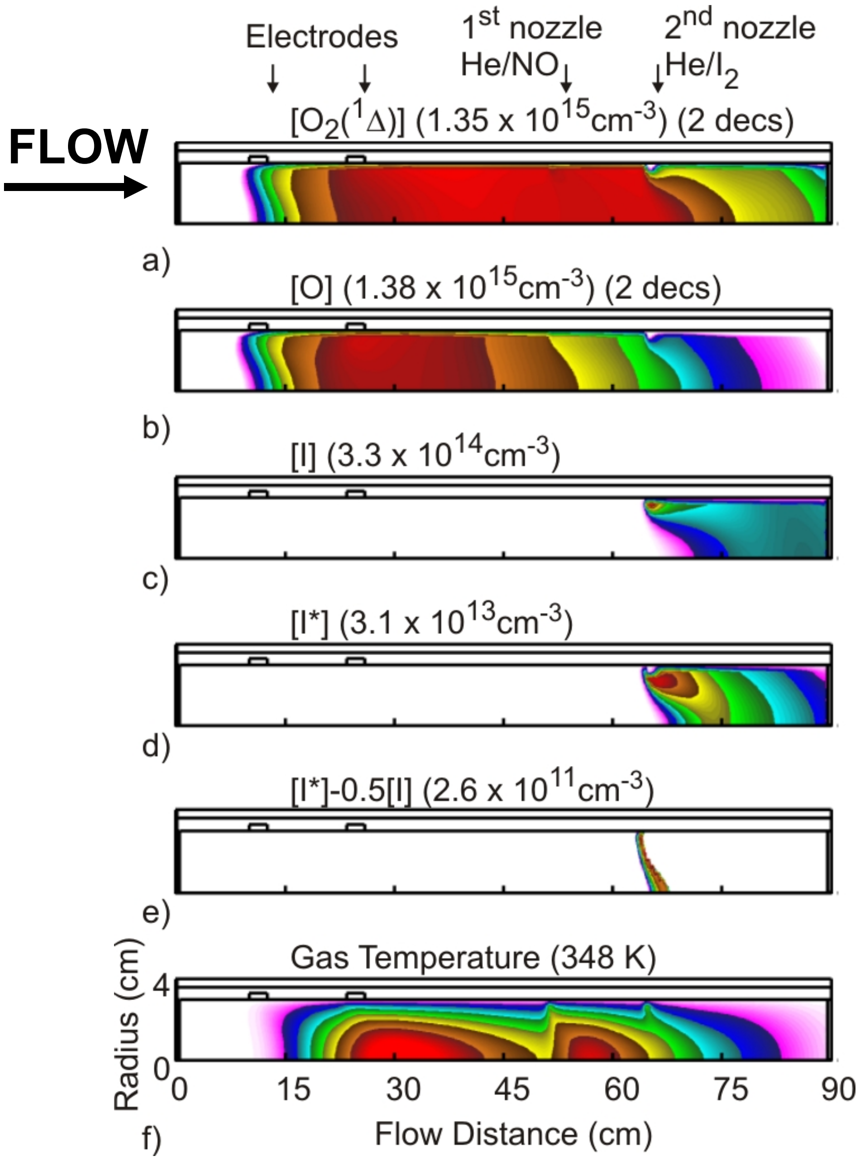


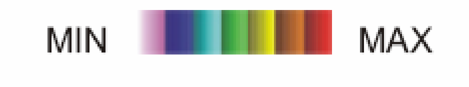
- T_e is higher than optimum value (1-1.5 eV).
- Addition of NO can lower T_e as ionization potential of NO is lower (9.26 eV).
- Density of negative ions need to be controlled as they can quench $O_2(^1\Delta)$.

$O^- + O_2(^1\Delta) \rightarrow O_3 + e^-$
$(k = 3 \times 10^{-10}\ cm^3\ s^{-1})$

- 6 lpm, 3 Torr, $He/O_2/NO$: 67/30/3, 40 W.

BASE CASE: NEUTRAL FLOW, DENSITIES





- $O_2(^1\Delta)$ is a long-lasting species, accumulates up to the I_2 injection.
- O is a quencher of upper level of laser.
- Complete dissociation of I_2 in these conditions.
- Second peak in T_g due to exothermic reaction between NO_2 and O.

$$NO_2 + O \rightarrow NO + O_2 \text{ (2 eV)}$$

- 6 slpm, He/O_2/NO:67/30/3, 40 W.
- 36 sccm, 100 % NO (1st nozzle).
- 100 sccm, 1% I_2 (2nd nozzle).

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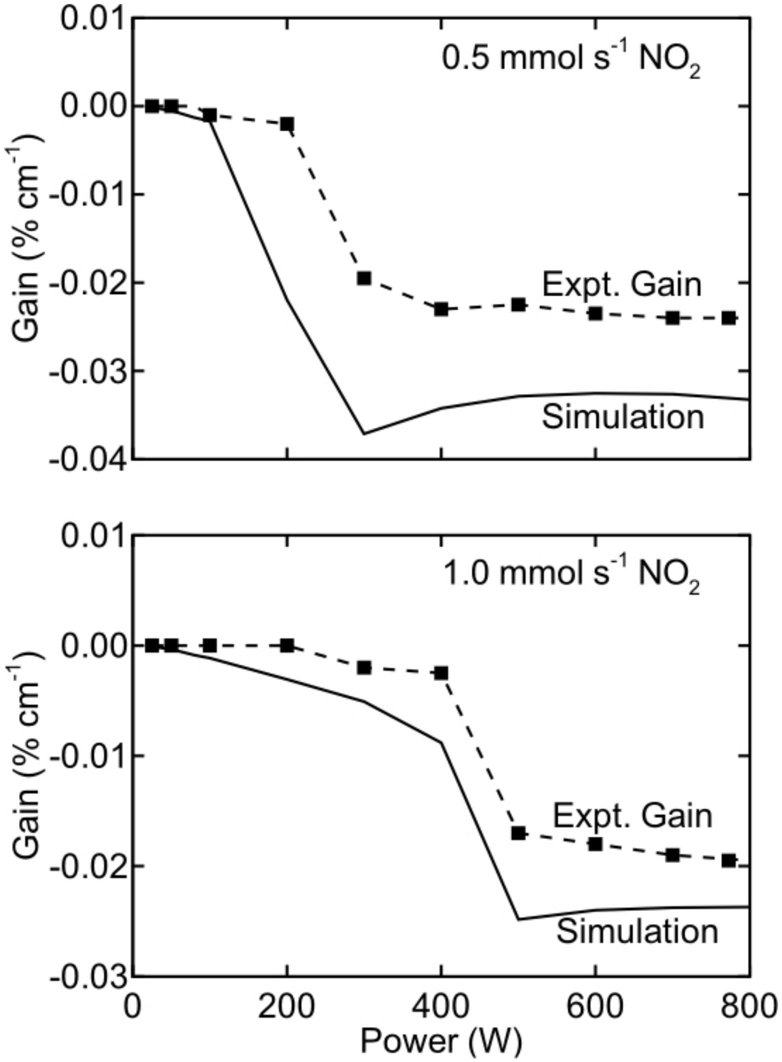
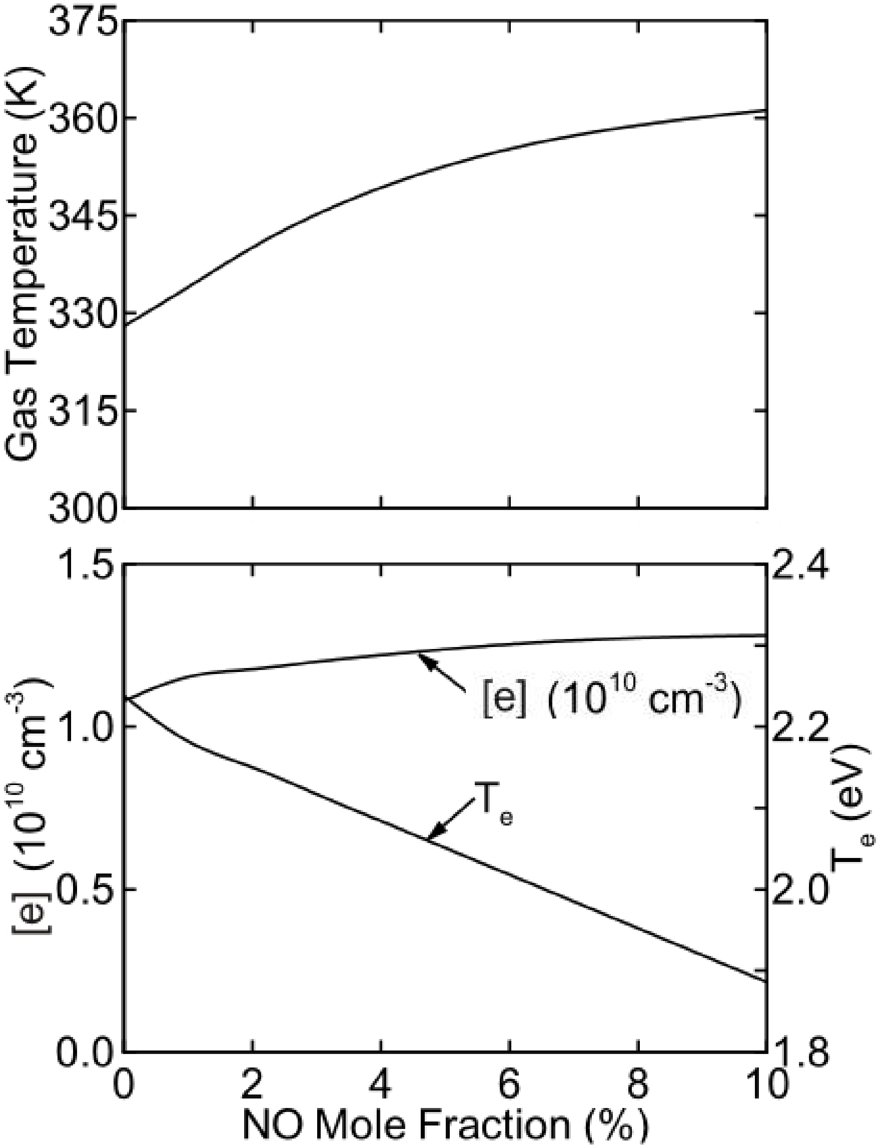
VALIDATION OF REACTION MECHANISM



- **10 Torr, He/O_2: 80/20, 20 mmol sec^{-1}**
- **Pure NO_2 through the 1st inlet.**
- **0.008 mmol s^{-1} I_2 through 2nd inlet.**
- **Diameter 4.9 cm, gain calculated at 10 cm downstream from I_2 injection (warm gas results in negative gain).**
- **At high powers, dissociation of O_2 (to O) causes reduction in yield.**
- **Addition of NO_2 recoups O atoms which would otherwise quench I^*.**

- **Ref: D. L. Carroll et al, IEEE J. Quantum Electron. 41, 213 (2000).**

NO ADDITION: PLASMA, TEMPERATURE



- [e] increases due to lower IP of NO (9.26 eV), recouping of -ve ions by NO.

  $NO + O^- \rightarrow NO_2 + e$

- Increase in T_{gas} due to exothermic reactions:

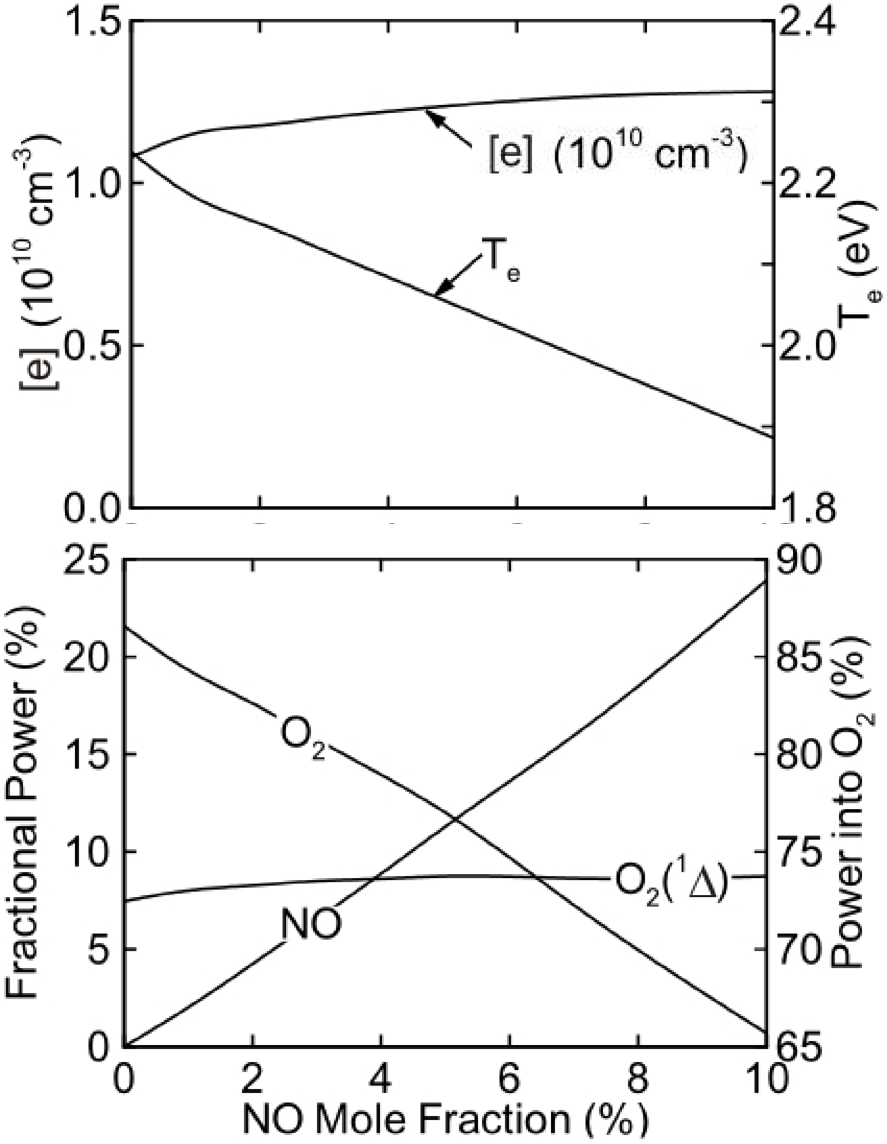
  $NO + O + M \rightarrow NO_2 + M$

  (308 kJ mol^{-1})

  $NO_2 + O \rightarrow NO + O_2$

  (193 kJ mol^{-1})

NO ADDITION: POWER INTO SPECIES



- Boltzmann calculations based on the T_e in the discharge.
- Power expended into NO increases linearly.
- Power expended in exciting $O_2(^1\Delta)$ remains a constant.
  - Decrease in power into O_2, but T_e is lower.
  - Excitation of $O_2(^1\Delta)$ efficient at lower T_e (1-1.5 eV).

NO ADDITION: O_2 ($^1\Delta$) and YIELD

- O(^{1}D) produces $O_2(^1\Delta)$ and $O_2(^1\Sigma)$ by collisions with O_2.
- [$O_2(^1\Delta)$] decreases due to quenching of O(^{1}D) by NO.

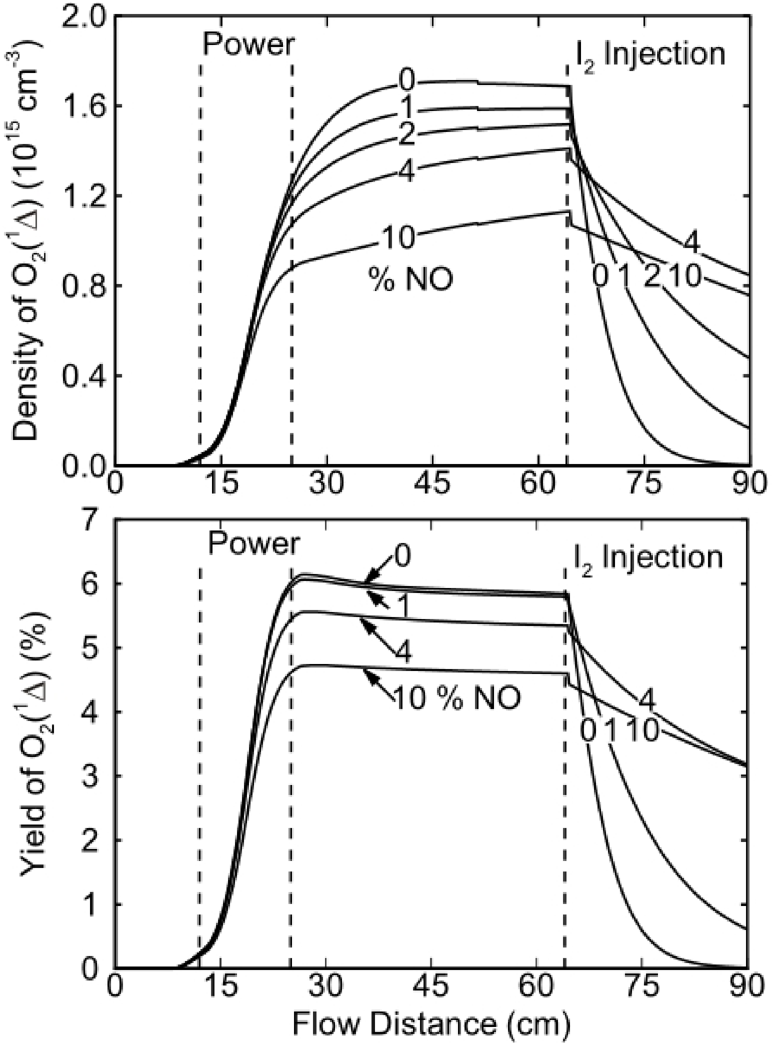
$O(^1D) + O_2 \rightarrow O_2(^1\Sigma) + O$ ($k = 2.6 \times 10^{-11}$)

$O(^1D) + O_2 \rightarrow O_2(^1\Delta) + O$ ($k = 1.5 \times 10^{-12}$)

$NO + O(^1D) \rightarrow NO + O$ ($k = 4.0 \times 10^{-11}$)

$NO_2 + O(^1D) \rightarrow NO + O_2$ ($k = 4.0 \times 10^{-10}$)

- Yield not very different for NO < 4%.



- Inlet: 6 lpm, 3 Torr, He/O_2/NO: 70-x/30/x, 40 W.
- 2nd nozzle: 100 sccm, 1% I_2.

EFFECT OF NO ADDITION: O AND $O_2(^1\Sigma)$

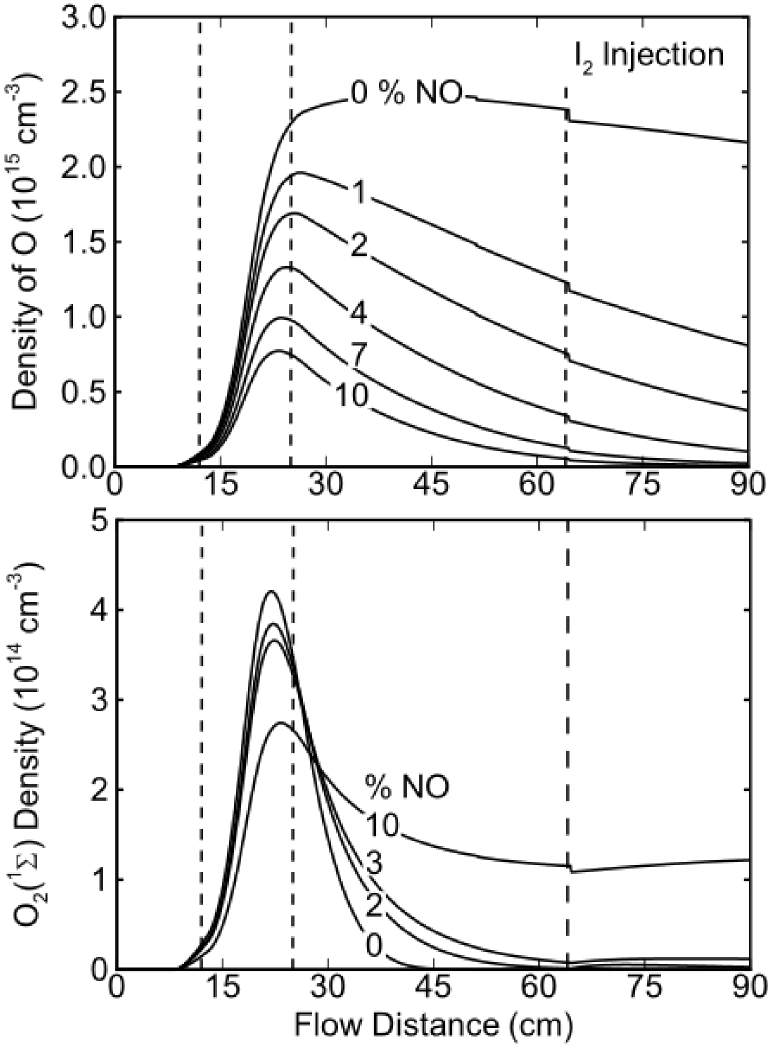
- **[O] rapidly decreases with NO addition due to recouping of O atoms by NO.**

$$\mathbf{NO + O + M \rightarrow NO_2 + M}$$

$$\mathbf{NO_2 + O \rightarrow NO + O_2}$$

- **$[O_2(^1\Sigma)]$ increases with NO addition due to lack of conversion of $O_2(^1\Sigma)$ to $O_2(^1\Delta)$.**

$$\mathbf{O + O_2(^1\Sigma) \rightarrow O + O_2(^1\Delta)}$$

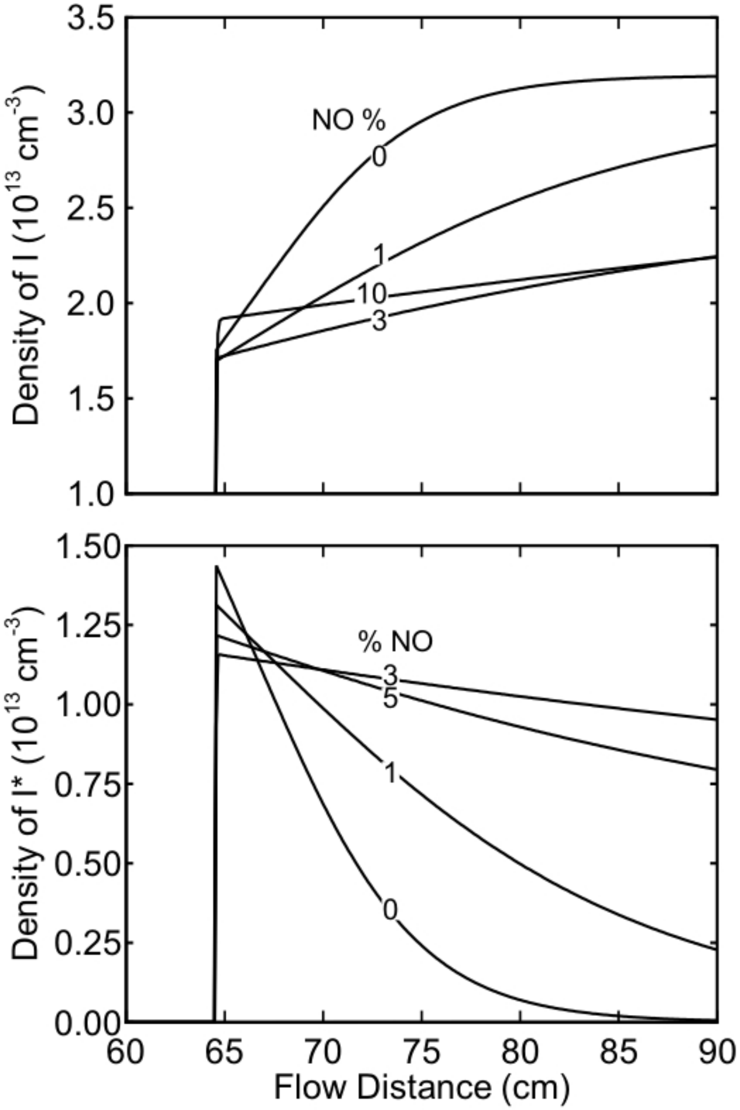


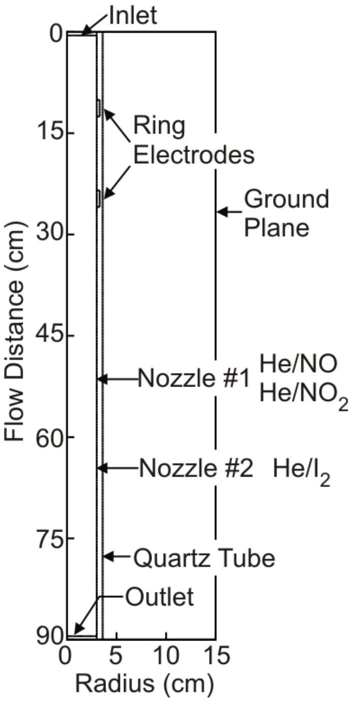
- **Inlet: 6 lpm, 3 Torr, He/O_2/NO: 70-x/30/x, 40 W.**
- **2nd nozzle: 100 sccm, 1% I_2.**

NO ADDITION: I AND I*

- **For large NO, [I] lower due to reduction in [O] that dissociates I_2 and quench I^*.**

- **For large NO mole fractions, Yield of $O_2(^1\Delta)$ is low, and hence $[I^*]$ is low.**





- **Inlet: He/O_2/NO: 70-x/30/x, 40 W.**
- **2nd nozzle: 100 sccm, 1% I_2.**

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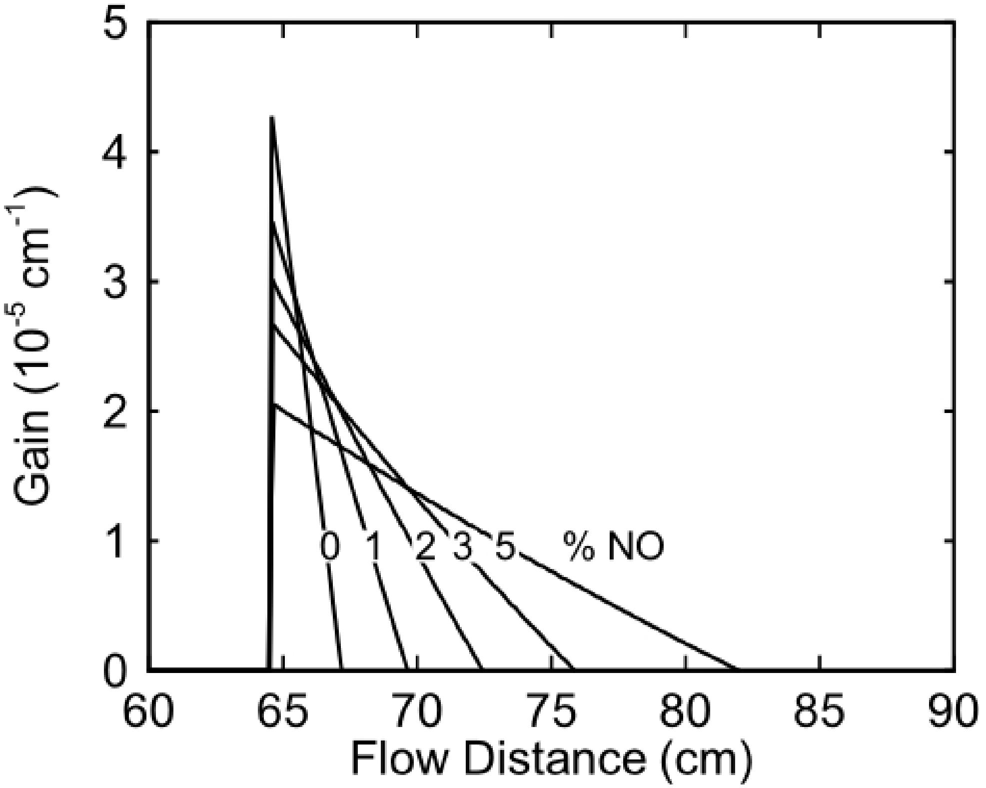
NO ADDITION: GAIN

- **At large NO mole fractions, positive gain extends over larger regions.**
- **Useful in optimizing optics and multi-pass resonators.**

$$\text{Gain} = \sigma([\text{I}^*] - 0.5[\text{I}])\ \text{cm}^{-1}$$

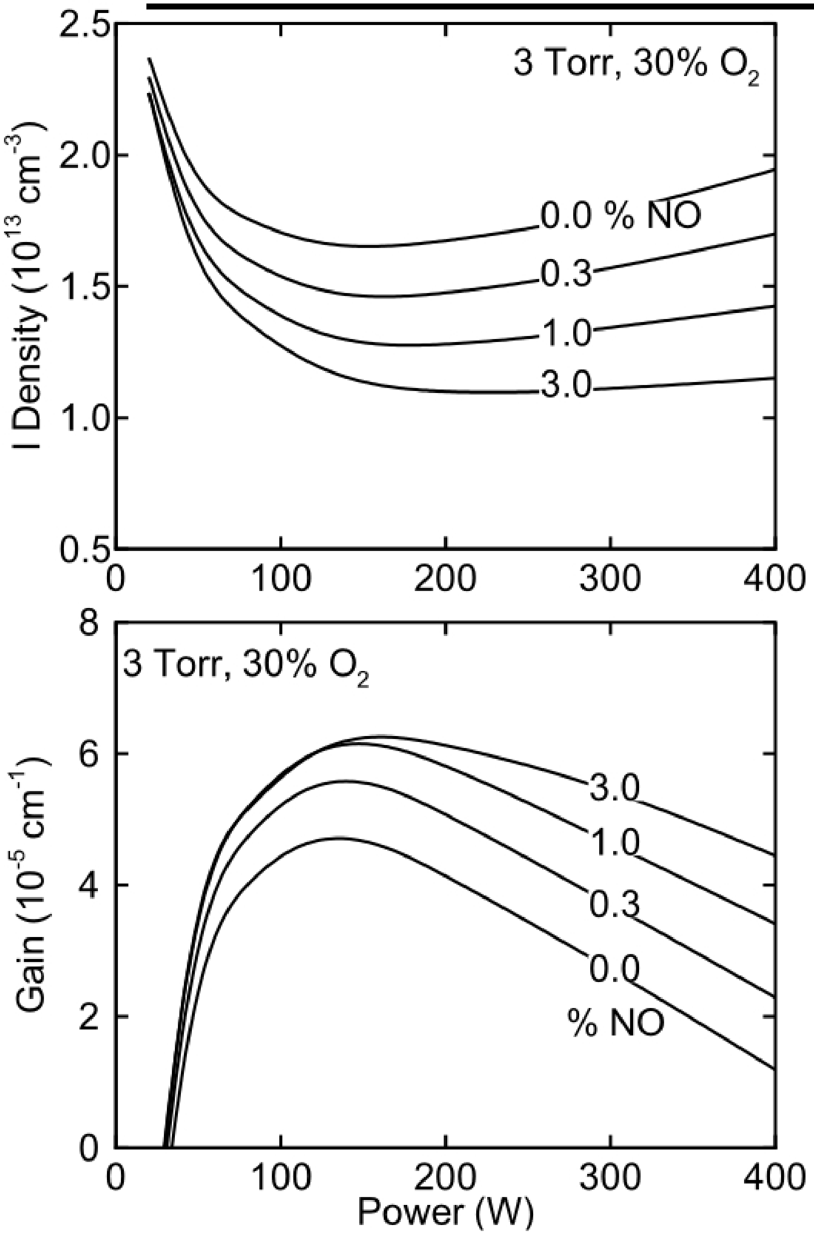
$$\sigma = \left(1.33 \times 10^{-16}\right)\sqrt{\frac{1}{T_g}}\ \text{cm}^2$$

- **Note: Mach 2 equivalent rate coefficients**



- **Inlet: 6 lpm, 3 Torr, He/O_2/NO: 70-x/30/x, 40 W.**
- **2nd nozzle: 100 sccm, 1% I_2.**

POWER, NO: EFFECT ON GAIN

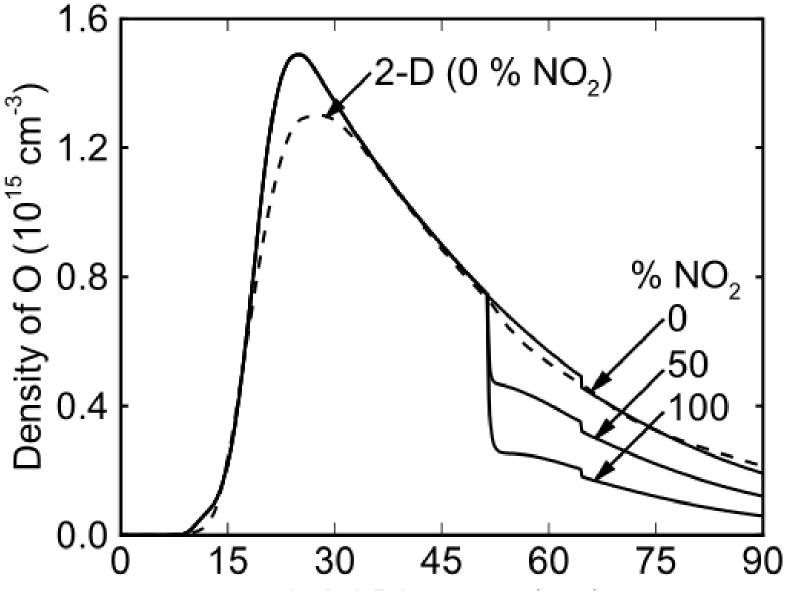


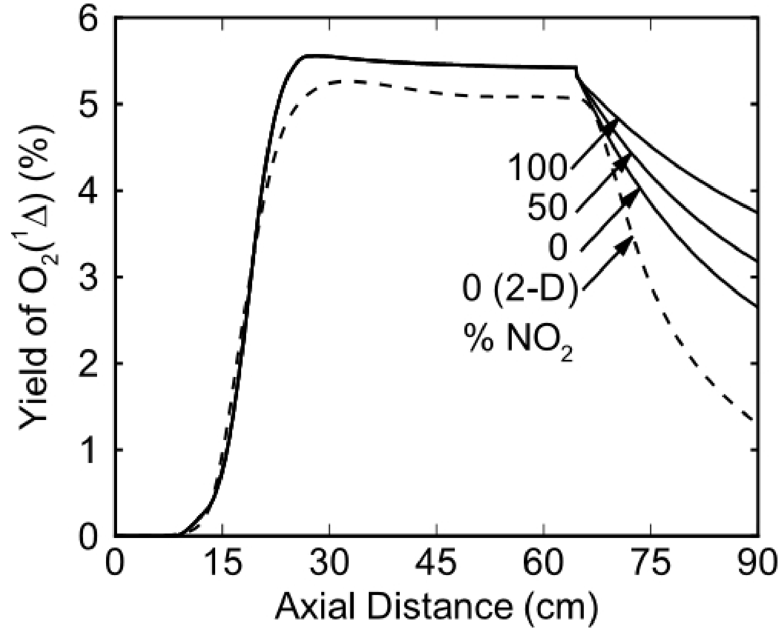
- Densities 2 cm downstream of I_2 injection.*
- Addition of NO most effective at high powers where [O] and the quenching by [O] are large.
- By recouping O atoms, feedstock of O_2 is maintained.

- Inlet: 6 lpm, 3 Torr, He/O_2/NO: 70-x/30/x.
- 2nd nozzle: 100 sccm, 1% I_2.

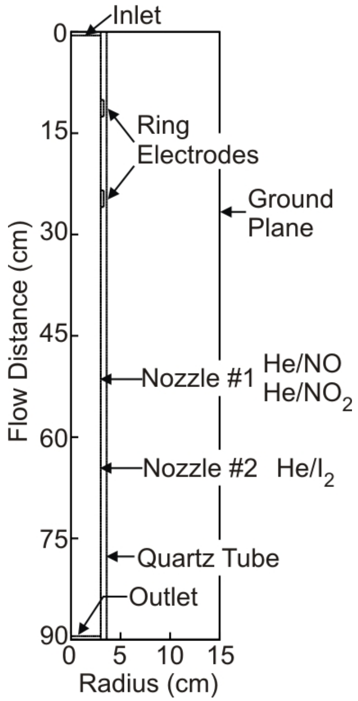
Ref: T.M.Muruganandam et al, AIAA J. 40, 1388 (2002).

NO$_2$: DENSITIES OF O, O$_2$($^1\Delta$)





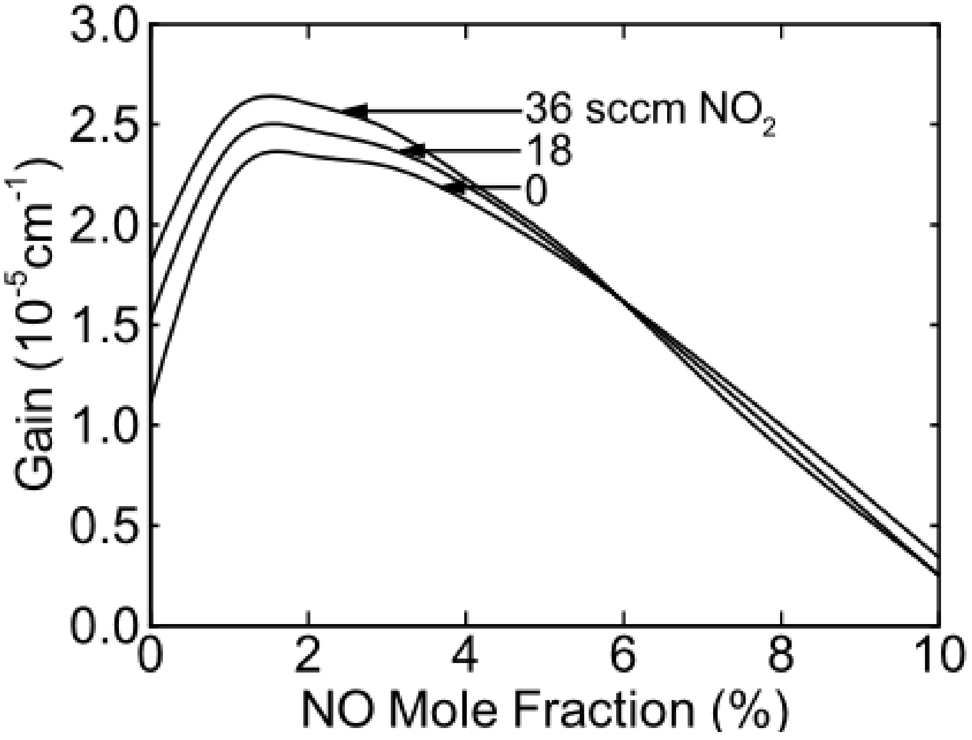
- NO$_2$ addition through 1st nozzle.
- NO$_2$ addition quickly consumes O atoms as the reaction of NO$_2$ and O is fast (2-body reaction).
- Increase in T_g lowers [O$_2$($^1\Delta$)] near 1st nozzle, but yield does not change.



- Inlet: He/O$_2$/NO: 67/30/3.
- 1st nozzle: 100 sccm, 1% I$_2$.

NO_2 : DENSITIES OF I, I^*, GAIN

- **Impact of NO_2 significant at low NO inlet mole fraction.**
- **At high NO mole fractions, yield of $O_2(^1\Delta)$ reduces thereby reducing $[I^*]$ and gain.**



- **Inlet: $He/O_2/NO$: 70-x/30/x.**
- **1st nozzle: He/NO_2 flow, 2nd nozzle: 1 sccm I_2.**

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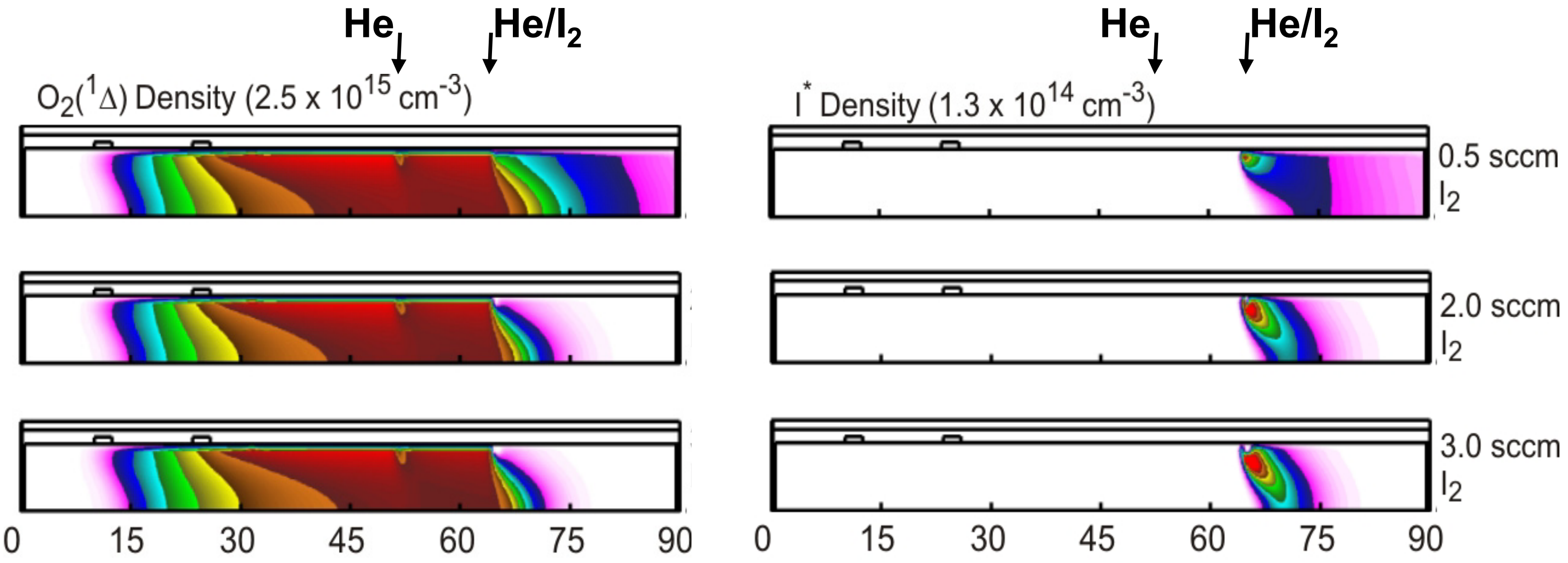
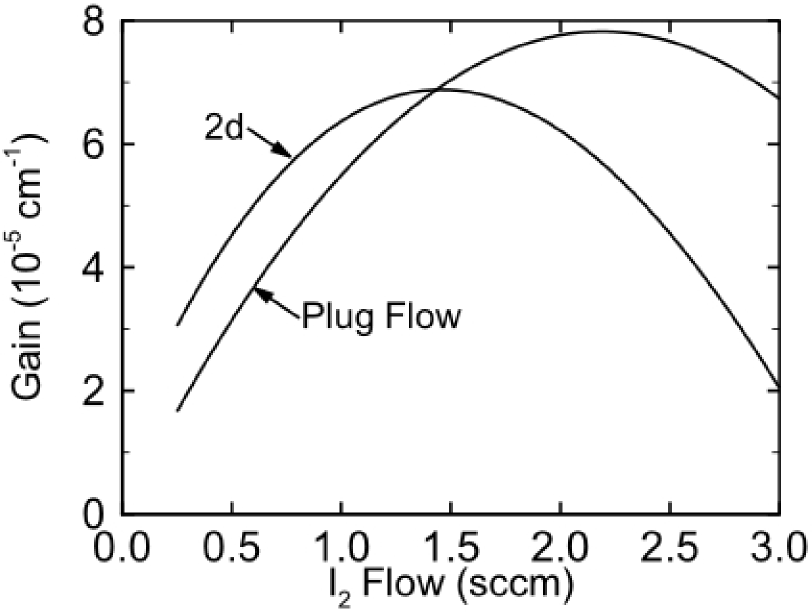
SCALING WITH I_2 FLOW: GAIN, $O_2(^1\Delta)$



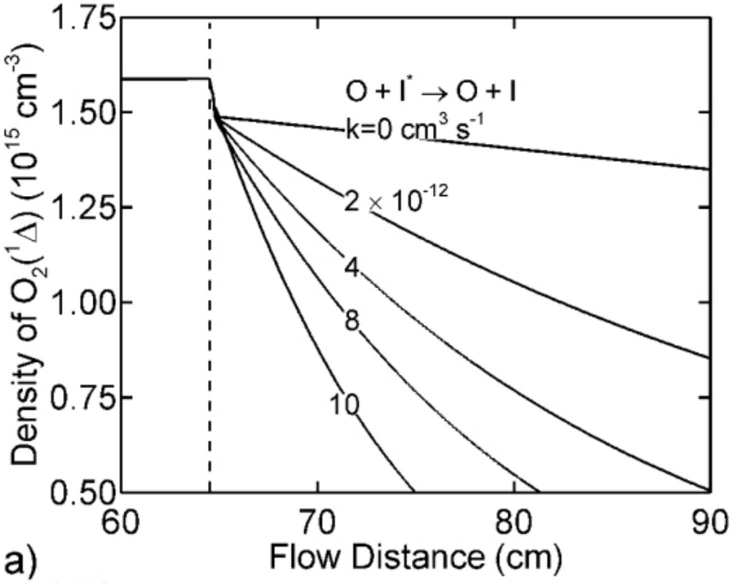


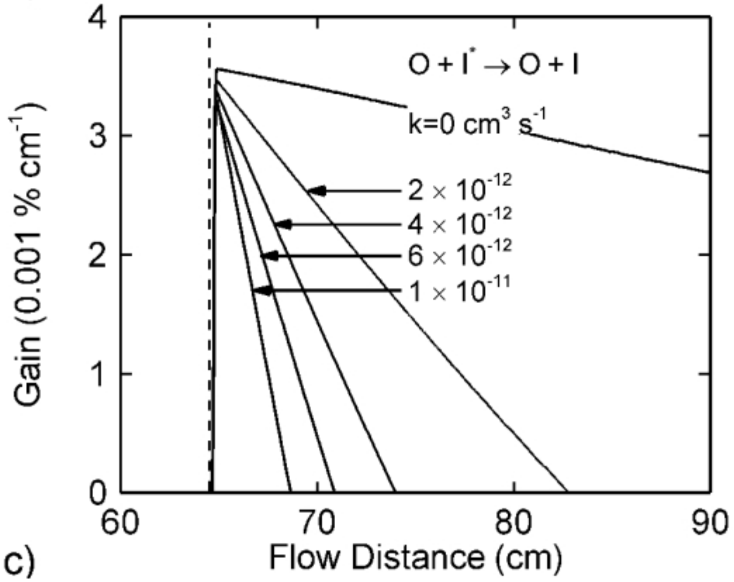
- Fast depletion of $O_2(^1\Delta)$ at high I_2 flows.
- For low I_2 flow, region of gain is larger.
- Optimal I_2 leads to higher gain.
    - $He/O_2/NO$: 68/30/2, 80 W
    - 2nd nozzle: 100 sccm, 1% I_2.

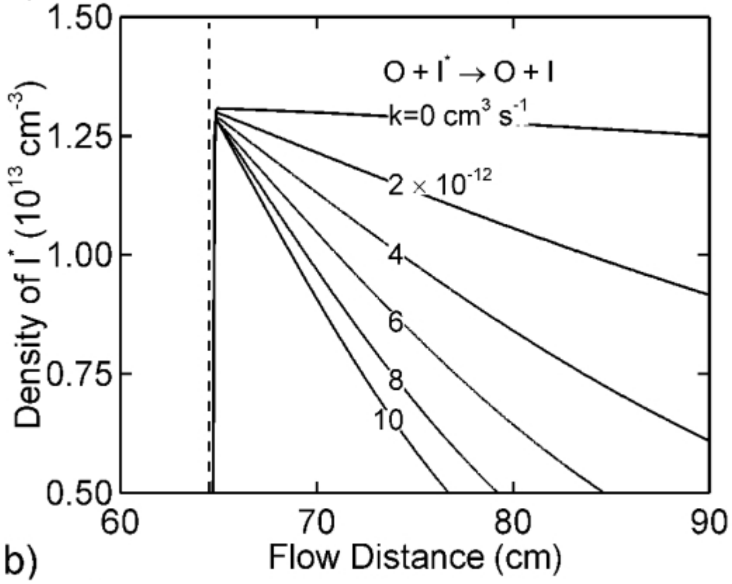
CONCLUDING REMARKS

- Production of $O_2(^1\Delta)$ in a He/O_2/NO discharge for use in eCOILs.
- Small amount of NO reduces the T_e and increases [e], both of which improve $O_2(^1\Delta)$ production.
- Consumption of O by NO is important when scaling to higher power, as it helps maintain feedstock of O_2.
- Small amounts of NO_2 prior to injection of I_2 help in quickly recouping O atoms which quench the upper level (I^*).

IMPORTANCE IN CONTROLLING DENSITY OF O







- **In the absence of quenching by O, [I^*] reaches an equilibrium value based on yield of $O_2(^1\Delta)$.**
- **Reduction of O helps in preserving the I^* and $O_2(^1\Delta)$ which increases the laser performance and improves robustness of the system.**

- **Inlet: He/O_2/NO: 67/30/3.**
- **2nd nozzle: 100 sccm, 1% I_2.**