Analytical OES

LIF OH



# Diagnostics on Plasma Chemistry: Unveiling Secrets

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#### Spectroscopic Diagnostics in Plasma Chemistry: Plasma parameters

Plasma parameters determine electron impact dissociation rates

The starting point of Plasma Chemistry

#### electron density

- Emission spectroscopy with absolute calibration with knowledge of the EEDF
- Lines ratio method based on a CR model including electron collision processes in electronic states
- Stark broadening
- Thomson scattering
- Laser Collision-induced fluorescence

### Spectroscopic Diagnostics in Plasma Chemistry: Plasma parameters

Plasma parameters determine electron impact dissociation rates

The starting point of Plasma Chemistry

electron energy distribution function  $(T_e?)$  - reduced electric field E/N

- Lines ratio method based on a CR model
- Stark polarization spectroscopy
- Thomson scattering
- Coherent Raman Scattering (CARS)

### Spectroscopic Diagnostics in Plasma Chemistry: vibrational excitation

Vibrational excitation affects dissociation rates and the discharge power balance

see, for example,  $CO_2$  and  $CH_4$  dissociation in plasma reforming issues or  $H_2$  dissociative ionization in negative ion sources

vibrational distributions in the ground state

- OES based on a CR model
- infrared emission spectroscopy (polar molecules)
- Raman Scattering (spontaneous and coherent CARS)

#### Spectroscopic Diagnostics in Plasma Chemistry: gas temperature

Important for processing and for the definition of operating conditions

based on the rotational temperature of emission bands

T<sub>gas</sub>=T<sub>rot</sub> ?

see P J Bruggeman, N Sadeghi, D C Schram and V Linss "Gas temperature determination from rotational lines in non-equilibrium plasmas: a review" Plasma Sources Sci. Technol. 23 (2014) 023001

#### Spectroscopic Diagnostics in Plasma Chemistry: transient species

Reaction intermediates: radicals, metastable electronic states

concentration, time evolution: actors and markers of the (plasma-)chemical kinetics, kinetic models validation

Techniques - preferably time-resolved

- OES based on a CR model
- absorption spectroscopy
- laser-induced fluorescence (LIF) spectroscopy

### **Optical Emission Spectroscopy (OES)**



 $\frac{collisional-radiative(CR) models}{\frac{dA^*}{dt} = R_{exc} - QA^*}$  Q = radiative. + collisional deexcitation

#### Analytical use of OES possible provided:

 $R_{exc}$  is a known function of A Q is known

# Absorption

## line of sight measurement - low spatial resolution

Conventional (resonant, broad-band), Cavity enhanced (CEAS-CRDS)



#### Laser Induced Fluorescence (LIF)

# pulsed lasers - high temporal and spatial resolution

 $10 \text{ ns} - \text{sub-mm}^3$ 



OH A-X POTENTIAL CURVES





Collision-induced transformations of electronic states –  $A^* + M \rightarrow B + M$ 

#### electronic quenching

The process by which a collision with specie M removes the energy from the excited state manifold towards any other final product





LIF thermometry

Collision-induced transformations of electronic states –  $A^* + M \rightarrow B + M$ 

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LIF OH A

Collision-induced transformations of electronic states –  $A^* + M \rightarrow B + M$ 

#### rotational energy transfers (RET)

# RET collisions are very fast

for N<sub>2</sub>( $B^{3}\Pi_{g}$ ):  $k^{RET} = 3 \times 10^{-9} cm^{-3} s^{-1}$   $k^{Q} = 3 \times 10^{-11} cm^{-3} s^{-1}$  $\tau^{RET} \approx 1/100\tau$ 



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 $\tau^{RET} \ll \tau$  $T_{rot} = T_{gas}$ 



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 $\tau^{\textit{RET}} \ll \tau$ 

 $T_{rot} = T_{gas}$ 

# ALWAYS TRUE ?



# The OH( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) 3064 Å System in He-H<sub>2</sub>O

 $\tau^{RET} \ll \tau$  not fulfilled, especially for J > 10, on increasing water content decrease of lifetime and strong decrease of RET rates on increasing J





Collision-induced transformations of electronic states –  $A^* + M \rightarrow B + M$ 

#### vibrational energy transfers (VET)

# VET collisions depend strongly on collision partner

for 
$$OH(A^2\Sigma^+, v = 1 \rightarrow v = 0)$$
:

$$k^{VET} \sim 10^{-14} cm^{-3} s^{-1}$$
 for He

$$k^{VET} = 2.7 imes 10^{-12} cm^{-3} s^{-1}$$
 for Ar

$$k^{VET} = 7.3 \times 10^{-11} cm^{-3} s^{-1}$$
 for H<sub>2</sub>O  
 $k^{VET} = 2.3 \times 10^{-10} cm^{-3} s^{-1}$  for N<sub>2</sub>



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# $\tau^{VET}/\tau$

Strongly dependent on gas mixture composition



#### heavy particles collisions

Sources: Combustion and atmospheric chemistry research

#### Electronic quenching - various colliders

NO( $A^2\Sigma^+$ ), OH( $A^2\Sigma^+$ ) and CH( $A^2\Delta$ ) in the temperature range 300-2500 K

 $N_2(C^3\Pi_u, v = 0 - 4), N_2^+(B^2\Sigma_u^+, v = 0, 1, 2)$ 

He n=3,4 sublevels, Ar n=4 sublevels

H(3d<sup>2</sup>D<sub>J</sub>), O(3p<sup>3</sup>P<sub>J</sub>), N(3s<sup>4</sup>P<sub>3/2</sub>) (for TALIF meas. of H, O, N), Kr(5p'[3/2]<sub>2</sub>), Xe(7p[3/2]<sub>2</sub>) (for calibration)

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#### VET - various colliders

 $CH(A^2\Delta, B^2\Sigma^-, v = 1)$ ,  $OH(A^2\Sigma^+, v = 1)$ , the  $N_2(C^3\Pi_u, v = 0 - 4)$  manifold

#### heavy particles collisions

Sources: Combustion and atmospheric chemistry research

Electronic quenching - various colliders

NO( $A^2\Sigma^+$ ), OH( $A^2\Sigma^+$ ) and CH( $A^2\Delta$ ) in the temperature range 300-2500 K

N<sub>2</sub>( $C^3\Pi_u, v = 0 - 4$ ), N<sub>2</sub><sup>+</sup>( $B^2\Sigma_u^+, v = 0, 1, 2$ )

He n=3,4 sublevels, Ar n=4 sublevels

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# Current knowledge on collision processes

electron collisions

#### Electronic quenching and collision transfers - various colliders

He n=3,4 sublevels,  $T_e < 1eV$ ,  $T_e = 3-7 eV$  - measurements

Ar n=4 sublevels - detailed balance from the inverse electron impact excitation



## **Optical Emission Spectroscopy (OES)**



collisional-radiative(CR) models

$$\frac{dA^*}{dt} = R_{exc} - QA^*$$

$$Q = \text{radiative.} + \text{collisional de-}$$
excitation

Analytical use of OES possible provided:

 $R_{exc}$  is a known function of A Q is known

#### Identification of excitation processes: pulsed discharges

The decay of the optical emission is an indication of the excitation process

with  $R_{exc} = 0$ ,  $\frac{dA^*}{dt} = -QA^*$ : exponential decay



N<sub>2</sub> Second Pos. Sys.

LIF N<sub>2</sub>(A)

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$$e + N_2(X^1\Sigma_g) \rightarrow N_2(C^3\Pi_u) + e$$

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Slow component

 $N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(C^3\Pi_u) + N_2(X)$ 

#### Emission - LIF Time-correlation: the NO- $\gamma$ System

# NO- $\gamma$ emission not due to electron impact excitation

SPS emission follows the electron impact time evolution N2 ATP Dielectric Barrier Discharge

Townsend diffuse discharge





#### Emission - LIF Time-correlation: the NO- $\gamma$ System

 $N_2(A^3\Sigma^+_u)$  by LIF and NO- $\gamma$  emission

 $N_2(A^3\Sigma_u^+) + NO(X) \rightarrow NO(A^2\Sigma^+) + N_2(X)$ 

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The George Clooney Criterion: WHAT ELSE?

Time correlation is a strong indication but not a rigorous proof. It must be supported by a knowledge of all possible processes.

in He - CH<sub>4</sub> (+small N<sub>2</sub> admix.)



FNS - 
$$N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$$
 as "acti-

Penning ionization:  $He(2^3S) + N_2(X) \rightarrow N_2^+(B) + He$ 

in He - CH<sub>4</sub> (+small N<sub>2</sub> admix.)



FNS -  $N_2^+(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$  as "actinometer"

Penning ionization:  $He(2^{3}S) + N_{2}(X) \rightarrow N_{2}^{+}(B) + He$ 

if CH(A) is excited by dissociative excitation (DE)

 $He(2^{3}S) + CH_{4} \rightarrow CH(A) + prod.$ 

in He - CH<sub>4</sub> (+small N<sub>2</sub> admix.)



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$$f_2 = \frac{I_{CHA}Y_{FNS}}{I_{FNS}Y_{CHA}} \frac{[N_2]}{[CH_4]} = \frac{r_{DE}}{r_{Penn}} \frac{[CH_4]}{[N_2]}$$

is a linear function of  $[CH_4]/[N_2]$ 

in He - CH<sub>4</sub> (+small N<sub>2</sub> admix.)



slope=
$$(1.73 \pm 0.07) \times 10^{-2}$$
  
 $\frac{r_{DE}}{r_{Penn}} = 1.95 \times 10^{-2}$  (literature)

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is a linear function of  $[CH_4]/[N_2]$ 

in  $N_2$  -  $CH_4\ mixtures$ 



SPS - 
$$N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$$
 as "actinome-  
ter"  
electron impact

$$e + N_2(X) \rightarrow N_2(C) + e$$

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in  $N_2$  -  $CH_4$  mixtures



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## Ratio of emission spectral features - the CH 4300 Å System

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$$F_3 = \frac{I_{CHA}Y_{SPS}}{I_{SPS}Y_{CHA}}[N_2] = \frac{r_{DE}}{r_{eC}}[CH_4]$$

is a linear function of [CH<sub>4</sub>]

## Ratio of emission spectral features - the CH 4300 Å System

#### in $N_2$ - $CH_4$ mixtures



slope=
$$(3.28 \pm 0.06) \times 10^{-2}$$
  
 $\frac{r_{DE}}{r_{eC}} = 2 \times 10^{-2}$  (EEDF calc.)

SPS -  $N_2(C^3\Pi_u \rightarrow B^3\Pi_g)$  as "actinometer"

electron impact

$$e + N_2(X) \rightarrow N_2(C) + e$$

if CH(A)is excited by DE

$$e + CH_4 \rightarrow CH(A) + prod.$$

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## VDF features: The $CN(B^2\Sigma^+ \rightarrow X^2\Sigma^+)$ Violet System

in  $N_2$ -CH<sub>4</sub> mixtures

suprathermal distribution overpopulation of v=1, 2, 3 not time-resolved measurements



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in pure  $N_2$  gas feed

suprathermal distribution

overpopulation of v up to v=7

#### not time-resolved measurements



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suprathermal distribution

overpopulation of v up to v=7

#### active role of the surface

carbon species from the surface deposit

#### not time-resolved measurements



Time (ms)

## Does CN(B) excitation involve CN(X) processes?



Time (ms)

Time (ms)

## VDF features: The CN( $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ) System

#### weak vibrational relaxation in the CN(B,v) manifold (LIF)

close to nascent CN(B,v) vibrational distributions - memory of the creation process

#### time-spectrally-resolved

In N<sub>2</sub> post-discharge



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In N<sub>2</sub> post-discharge



in N<sub>2</sub>-CH<sub>4</sub> discharge













## VDF features: The CN( $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ) System

based on vibrational distributions + a pinch of GC (WHAT ELSE?) criterion

 $C + N + M \rightarrow CN(B) + M$ Washida et al. 1975 J. Chem Phys. 63

4230



## VDF features: The CN( $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ ) System

based on vibrational distributions + a pinch of GC (WHAT ELSE?) criterion

 $\frac{C + N + M \rightarrow CN(B) + M}{\text{Washida et al. 1975 J. Chem Phys. 63}}$ 

 $N + CH \rightarrow CN(A, B) + H$  $(N + CH_2 \rightarrow CN(A, B) + H_2)$ reaction exhothermicity





## Identification of excitation processes: pulsed discharges

The decay of the optical emission is an indication of the excitation process

with  $R_{exc} = 0$ ,  $\frac{dA^*}{dt} = -QA^*$ : exponential decay



N<sub>2</sub> Second Pos. Sys.

fast component

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Slow component

 $N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \rightarrow N_2(C^3\Pi_u) + N_2(X)$ 

LIF N<sub>2</sub>(A)

## Identification of excitation processes: pulsed discharges

#### And the vibrational distribution too!!



**Figure 10.** Post discharge evolution of the normalized  $[N_2(G, \nu)]$  distribution at  $p \approx 0.5$  Torr.  $t_{pd}$  is the post discharge time (from [37]).

#### fast component

$$e + N_2(X^1\Sigma_g) \rightarrow N_2(C^3\Pi_u) + e$$

intermediate component
$$e + N_2(A^3\Sigma^+_\mu) o N_2(C^3\Pi_\mu) + e$$
 slow e

#### Slow component

$$N_2(A^3\Sigma_u^+) + N_2(A^3\Sigma_u^+) \to N_2(C^3\Pi_u) + N_2(X)$$

## Rot. excitation: the OH( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) System

Emission spectra show over-thermal ro-vibrational excitation He-H<sub>2</sub>O discharge



Exp

Sim

100

## Rot. excitation: the OH( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) System

Rotational excitation depends on the vibrational level

and on water partial pressure







(0,0)

wavelenght (Å)

## Rotational excitation: the OH( $A^2\Sigma^+ \rightarrow X^2\Pi$ ) System

Fingerprints of an exothermic process - Perhaps (in He-H<sub>2</sub>O) disch.:

dissociative excitation  $H_2O + e \rightarrow OH(A) + e$ dissociative recombination  $H_2O^+(H_3O)^+ + e \rightarrow OH(A) + H(H_2)$ 



# E/N from N<sub>2</sub> Second Positive System (SPS) and First Negative System (FNS) emission ratio



model for (C,v=0) and (B,v=0)  

$$\frac{dC_0}{dt} = n_e k_0^{XC} X - (k_0^{QC} X + A_0^C) C_0$$

$$\frac{dB_0^+}{dt} = n_e k_0^{XB+} X - (k_0^{QB+} X + A_0^{B+}) B_0^-$$

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two resonant photons absorption

 $N_2(A^3\Sigma^+_u) + h\nu_{l1} \rightarrow N_2(B^3\Pi_g) + h\nu_{l2} \rightarrow N_2(C^3\Pi_u)$ 

fluorescence

 $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu_f$ 





**Direct fluorescence** 

electronic quenching rates









# E/N from N<sub>2</sub> Second Positive System (SPS) and First Negative System (FNS) emission ratio



model for (C,v) and (B,v=0) includes collision quenching and vibrational relaxation  

$$\frac{dC_v}{dt} = n_e k_v^{XC} X - (k_v^{QC} X + A_v^C) C_v + \sum_w k_{wv} X C_w}{\frac{dB_0^+}{dt}} = n_e k_0^{XB+} X - (k_0^{QB+} X + A_0^{B+}) B_0^+$$

Introduction

## $N_2^+(B, v = 0)$ electronic quenching

#### rate constants show a dependence on the excitation method class

Need for deeper investigation. Averaging over all data is probably not correct



# E/N determination by intensity ratio of SPS and FNS spectral bands: effect of $N_2^+(B)$ quenching incertitude

electron impact  

$$e + N_2(X) \rightarrow N_2(C, v) + e \qquad k_v^{XC}$$
  
 $e + N_2(X) \rightarrow N_2^+(B, v) + e \qquad k_v^{XB+}$ 

 $\frac{\text{steady-state v=0 emissions ratio}}{R = \frac{k_0^{XC}}{k_0^{XB+}} = \frac{I_{SPS}}{I_{FNS}} \frac{(k_0^{QC} X + A_0^C)}{(k_0^{QB+} X + A_0^{B+})}$ 



Three uncertainty cases are presented, with R varying by a factor of 3

## Model calculation of N<sub>2</sub>(C,v) populations

model includes collision quenching and vibrational relaxation

$$rac{dC_v}{dt} = n_e \sum_j k_{vj}^{XC} X_j - (k_v^{QC} X + A_v) C_v + \sum_w k_{wv} X C_w$$

electronic quenching by  $N_2$  - (OODR-LIF) and by  $O_2$  (pulsed discharge)

rate constants  $(10^{-11} cm^3 s^{-1})$ 

| coll           | v=0  | v=1  | v=2  | v=3  | v=4  |
|----------------|------|------|------|------|------|
| N <sub>2</sub> | 1.24 | 3.14 | 4.28 | 6.34 | 9.86 |
| O <sub>2</sub> | 30   | 31   | 37   | 43   | -    |



## Model calculation of N<sub>2</sub>(C,v) populations

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Introduction

(Analytical OES)

#### Vibrational Temperature of the ground state - SPS case



Old quenching data (w-out VET)  $T_e = 1.2 \text{ eV } T_v(X)=1100 \text{ K}$  $T_e = 1.7 \text{ eV } T_v(X)=300 \text{ K}$ 

New quenching data with VET

 $T_e = 3 \text{ eV} T_v(X) = 1100 \text{ K}$ 



#### Vibrational Temperature of the ground state - FNS case

#### Penning ionization in He-N2 mixtures

$$He(2^3S) + N_2(X^1\Sigma_g, v) \rightarrow N_2^+(B^2\Sigma_u^+) + e + He$$



Figure 8. Spectra of  $\Delta v = -2$  sequence of N<sub>2</sub><sup>4</sup>(FNS) for 0.2% N<sub>2</sub> mixture at 0.5 Torr and 500 Hz pulsing, in discharge (a) at 970 gs after the switching ON, and in post discharge (b) at 10 gs after the switching OFF.



Figure 13. N<sup>2</sup><sub>1</sub>(8,  $\tau$ ) relative vibrational distributions: experimental (symbol); referring also to the distributions of figure 14, (1) is generated from a Treanor-Gordiets N<sub>2</sub>(X,  $\sigma$ ) distribution at  $\tau_{\tau}$ =350 K and  $\theta_{\tau}$ =4150 K,  $\tau_{\tau_{\tau}}$ = $\sigma$ =1000 K curve (17); (2) from modified Treanor-Gordiets curve (27); (3) from modified Treanor Gordiets curve (37); (4) from Boltzmann at 4150 K curve (47).

Introduction

#### Vibrational Temperature of the ground state - FNS case

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Figure 14.  $N_3(X, v)$  relative distribution: experimental obtained from  $N_2^1(B, v')$  by matrix inversion (Symbols); (1) analytical Treanor-Gordiest distribution for  $T_1 = 330$  K, and  $\Theta_1^0 = 4150$  K,  $T_{xyy0} = 1000$  K; (2) as (1) but smoothing the curve for  $N_{xyy0}$ ; as curve (1) but  $T_{xyy0} = 1000$  K; (4) Boltzmann distribution at 4150 K.



Figure 13. N<sub>2</sub>(0, p') relative vibrational distributions: experimental (symbols); referring also to the distributions of figure 14, (1) is generated from a Treanor-Gordiets N<sub>2</sub>(X,  $p_1$ distribution at T<sub>1</sub>=350 K and  $\Theta_1$ =4150 K, T<sub>1>2</sub>=0=1000 K curve (1); (2) from modified Treanor-Gordiets curve (2); (3) from modified Treanor-Gordiets curve (3); (4) from Boltzmann at 4150 K curve (4).

## Analytical use of OES: conclusions

#### Is it possible to use OES for analytical purposes? (in particular radicals detection)

• electron impact does not always dominate the emission spectra

#### LIF N<sub>2</sub>(A)

## Analytical use of OES: conclusions

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#### Is it possible to use OES for analytical purposes? (in particular radicals detection)

- electron impact does not always dominate the emission spectra
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- excitation and quenching processes must be carefully known
- even the use of emission features as process monitor must be very careful, when not impossible

#### radicals monitoring must rely on other techniques

- Laser Induced Fluorescence
- Absorption

Introduction

(LIF OH)

## Laser Induced Fluorescence (LIF)

## pulsed lasers - high temporal and spatial resolution

 $10 \text{ ns} - \text{sub-mm}^3$ 



OH A-X POTENTIAL CURVES



Absorption

# LIF detection of OH

(LIF OH)

## absorption

| он(>       | <²П <sub>i</sub> ) | +   | $h\nu_L$        | $\rightarrow$ |     | OH(A            | $^{2}\Sigma^{+})$ |
|------------|--------------------|-----|-----------------|---------------|-----|-----------------|-------------------|
| $\Delta v$ | =                  | 1   | seque           | nce           | -   | (1,0)           | band              |
| Q1(1)      | +Q21               | (1) | lines $\lambda$ | = 2           | 281 | .913 <i>n</i> ı | m                 |



# LIF detection of OH

#### absorption

 $OH(X^2\Pi_i) + h\nu_L \rightarrow OH(A^2\Sigma^+)$   $\Delta\nu = 1$  sequence - (1,0) band Q1(1)+Q21(1) lines  $\lambda = 281.913nm$ 

#### fluorescence

 $\begin{array}{rcl} OH(A^2\Sigma^+) & \rightarrow & OH(X^2\Pi_i) \ + \ h\nu_F \\ \Delta\nu & = \ 0 \ \ \text{sequence} \ \ (1,1)+(0,0) \ \ \text{bands} \\ \lambda \ \sim \ 310 nm \end{array}$ 



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# Model description of LIF process

The measured LIF signal

$$S(t) = \frac{\Omega}{4\pi} T \eta e GR(A_{(0,0)} P_{A0}(t) + A_{(1,1)} P_{A1}(t)) = \frac{S_0(t) + S_1(t) - PMT}{S_0(t) + S_1(t) - PMT}$$

 $\mathcal{J} = \int_0^\infty S(t) dt = \frac{\mathcal{J}_0 + \mathcal{J}_1 - \mathsf{ICCD}}{\mathcal{J}_0 + \mathcal{J}_1 - \mathsf{ICCD}}$ 





Introduction

# Model description of LIF process

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#### The dance of collisions in fluorescence spectra

# Beauty, as well as happiness, is frequent. No day goes by without we live a little while in paradise.

Jorge Luis Borges

(LIF OH) Abso

# The VET versus $Q_E$ competition determines fluorescence features: the Ar-H<sub>2</sub>O case

| rate                          | coefficients          |  |  |  |  |
|-------------------------------|-----------------------|--|--|--|--|
| $(cm^3s^{-1})$                |                       |  |  |  |  |
| $k_{Ar}^{1  ightarrow 0} =$   | $2.7 \times 10^{-12}$ |  |  |  |  |
| $k^{1\rightarrow 0}_{H_2O} =$ | $7.3 \times 10^{-11}$ |  |  |  |  |
| $k_{H_2O}^{Q_E} = 6.$         | $6 	imes 10^{-10}$    |  |  |  |  |

| VET              | Yield       |   |   |
|------------------|-------------|---|---|
|                  | $k^{VET}$   |   |   |
| k <sup>VET</sup> | $+ k^{Q_E}$ | + | A |

 $He + H_2O + air$ 

## Q + VET measurement allows recovering the gas composition

model calculations of: 
$$\mathcal{J}_0/\mathcal{J}_1$$
 and  $Q = \frac{\mathcal{J}_0 Q_0 + \mathcal{J}_1 Q_1}{\mathcal{J}_0 + \mathcal{J}_1}$ 



The gas composition is a single-valued  $f(\mathcal{J}_0/\mathcal{J}_1, Q)$ 

Introduction

Analytical OES

(LIF OH) AL

Absorption

LIF N<sub>2</sub>(A)

# LIF on OH in an APPJ - water interface space-dependent He-air-water mixture





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#### air and water from quenching and vibrational relax.

laser beam dia. = 0.1 mm (focussed) - observation slit = 0.1 mm



## Parallel plates Dielectric Barrier Discharge DBD



(LIF OH) A

## Possible interference from photochemical processes

Ozone photodissociation (no O<sub>3</sub> expected in He/Ar H<sub>2</sub>O discharges)

 $O_3 + h \nu_L \rightarrow O(^1D) + O_2$ 

 $O(^{1}D) + H_{2}O \rightarrow 2OH$ 

Hydrogen peroxide photodissociation

 $H_2O_2 + h\nu_L \rightarrow 2OH$ 

(LIF OH) Abs

## Possible interference from photochemical processes

Ozone photodissociation (no  $O_3$  expected in He/Ar  $H_2O$  discharges)

 $O_3 + h \nu_L 
ightarrow O(^1D) + O_2$ 

 $O(^1D) + H_2O \rightarrow 2OH$ 

## Hydrogen peroxide photodissociation

 $H_2O_2 + h\nu_L \rightarrow 2OH$ 

 $[H_2O_2]{=}780~ppm$   $\Rightarrow$  LIF signal 200 times lower than in the discharge

- 50% hydrogen peroxide solution in the bubbler
- no discharge

## The rotational excitation of OH ground state

## LIF excitation spectrum

## $H_2O_2$ photo-dissociation

| suprathermal                      |           |       | rotational | distr       | distribu- |  |
|-----------------------------------|-----------|-------|------------|-------------|-----------|--|
| tion                              | (1530     | Κ     | nascent    | temperat    | ure)      |  |
| but st                            | rongly re | laxed | by RET,    | even within | the       |  |
| short duration of the laser pulse |           |       |            |             |           |  |



## The rotational excitation of OH ground state

| in He-H <sub>2</sub> O discharge                 |                                |              |  |  |  |
|--|--------------------------------|--------------|--|--|--|
| thermal  | nermal rotational distribution |              |  |  |  |
| due to the long lifetime of OH                   |                                |              |  |  |  |
|  |                                |              |  |  |  |
| H <sub>2</sub> O <sub>2</sub> photo-dissociation |                                |              |  |  |  |
| suprathermal                                     | rotational                     | distribu-    |  |  |  |
| tion (1530                                       | K nascent                      | temperature) |  |  |  |
| but strongly relaxed by RET, even within the     |                                |              |  |  |  |
| short duration of the laser pulse                |                                |              |  |  |  |

## LIF excitation spectrum



## The rotational excitation of OH ground state

| in He-H <sub>2</sub> O discharge             |                                |              |  |  |  |
|--|--------------------------------|--------------|--|--|--|
| thermal                                      | hermal rotational distribution |              |  |  |  |
| due to the long lifetime of OH               |                                |              |  |  |  |
|  |                                |              |  |  |  |
| $H_2O_2$ photo-dissociation                  |                                |              |  |  |  |
| suprathermal                                 | rotational                     | distribu-    |  |  |  |
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| but strongly relaxed by RET, even within the |                                |              |  |  |  |
| short duration of the laser pulse            |                                |              |  |  |  |

## LIF excitation spectrum



#### LIF N<sub>2</sub>(A)

## OH decay in the post-discharge

$$OH + OH \rightarrow H_2O + O$$

$$OH + OH + M \rightarrow H_2O_2 + M \qquad k_{quad} = 5.2 \times 10^{-12} cm^3 s^{-1} \text{ at } P = 760 \text{ Torr}$$

$$\frac{d[OH]}{dt} = -2k_{quad} [OH]^2$$



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## OH decay in the post-discharge

$$\begin{array}{l} OH + OH \rightarrow H_2O + O \\ OH + OH + M \rightarrow H_2O_2 + M \\ \hline \frac{d[OH]}{dt} = -2k_{quad}[OH]^2 \end{array} k_{quad} = 5.2 \times 10^{-12} cm^3 s^{-1} \text{ at } \mathbf{P} = \mathbf{760 \ Torr} \end{array}$$





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## OH decay in the post-discharge

$$\begin{array}{l} OH + OH \rightarrow H_2O + O \\ OH + OH + M \rightarrow H_2O_2 + M \\ \hline k_{quad} = 5.2 \times 10^{-12} cm^3 s^{-1} \text{ at } \mathsf{P} = \mathbf{760 \ Torr} \\ \hline \frac{d[OH]}{dt} = -2k_{quad} [OH]^2 - \left(\sum_i k_i [X_i] + C\right) [OH] \quad \text{with} \quad \sum_i k_i [X_i] = K_i e^{-bt} \end{array}$$



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$$\begin{array}{l} OH + OH \rightarrow H_2O + O \\ OH + OH + M \rightarrow H_2O_2 + M \\ \frac{d[OH]}{dt} = -2k_{quad}[OH]^2 - \left(\sum_i k_i[X_i] + C\right)[OH] \quad \text{with} \quad \sum_i k_i[X_i] = K_i e^{-bt} \end{array}$$



LIF OH (

## Time-Resolved Broad-Band Absorption Spectroscopy (TR-BBAS) born as an OH LIF calibration technique



## Time-Resolved Broad-Band Absorption Spectroscopy (TR-BBAS)

$$\frac{I_{\lambda}^{M}(l,\lambda)}{I_{\lambda}^{M}(0,\lambda)} = \int_{+\infty}^{-\infty} exp\left[-IN_{ave}\sum_{i} n_{i}\sigma^{L}(\lambda_{i})\mathcal{L}(\lambda'-\lambda_{i})\right]\mathcal{S}^{N}(\lambda'-\lambda)d\lambda'$$



## Time-Resolved Broad-Band Absorption Spectroscopy (TR-BBAS)

minimum detectable density =  $(4-5) \times 10^{12} cm^{-3}$ 

l = 55 mm, gate = 100  $\mu$ s, input slit = 100  $\mu$ s, average = 10000, meas. time  $\sim$  18 min.



LIF OH (

## TR-BBAS improvements for a stand-alone technique

## timing scheme (ICCD) and LED collimation

for a better rejection of discharge emission and for multi-pass implementation



LIF OH AL

## TR-BBAS improvements for a stand-alone technique

## timing scheme (ICCD) and LED collimation

for a better rejection of discharge emission and for multi-pass implementation



## OH density in He-H<sub>2</sub>O-O<sub>2</sub> DBD

electrodes gap = 4.5 mm

electrodes gap = 2 mm





LIF N<sub>2</sub>(A)

### LIF + TR-BBAS = powerful tool!

## OH density and post-discharge kinetics

## Effect of the discharge duration (T<sub>ON</sub>) - Ar-H<sub>2</sub>O pulsed DBD



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Introduction

Analytical OES

LIF OH

(Absorption)

# LIF + TR-BBAS = powerful tool!

## Electron gun: calibrated OH maps



# Playing with gun parameters (flux, target NO - YES - material)

metal target

## no target (free jet expansion)





# Playing with gun parameters (flux, target NO - YES - material)

## metal target flux= 0.5 l/s

## metal target flux = 1 l/s





# Playing with gun parameters (flux, target NO - YES - material)

## dist. water target flux= 1 l/s

## metal target flux = 1 l/s





# Playing with gun parameters (flux, target NO - YES - material)

## dist. water target flux= 1 l/s



dist. water target flux= 2 l/s





#### Fixed laser wavelength

Absorption by  $Q_1(1)$  and  $Q_{21}(1)$ 

Fluorescence spectrum - collisionless






## Single wavelength LIF thermometry - OH - collisional case

#### xed laser wavelength

Absorption by  $Q_1(1)$  and  $Q_{21}(1)$ 

Fluorescence spectrum - collisional





## Single wavelength LIF thermometry - OH - collisional case

### $K_{RET}/K_Q$

number of RET collisons within the lifetime as a function of air partial pressure in He Fluorescence spectrum - collisional







## Single wavelength LIF thermometry - NO - collisionless case

#### Fixed laser wavelength

Simultaneous absorption by R<sub>22</sub>(2.5) and P<sub>22</sub> (13.5)

transitions of NO- $\gamma$  (0,0) band



Fluorescence spectrum - collisionless

(0,2) band, 0.1 Torr O2 pressure



## Single wavelength LIF thermometry - NO - collisionless case

#### Fixed laser wavelength

Simultaneous absorption by R22(2.5) and P22 (13.5)

transitions of NO- $\gamma$  (0,0) band

Fluorescence spectrum - collisionless



restricted to three spectral features





## Single wavelength LIF thermometry - NO - collisionless case

#### Sensitivity

 $S = \left(\frac{dT}{T}\right) / \left(\frac{dR_{21}}{R_{21}}\right)$ 



Fluorescence spectrum - collisionless

restricted to three spectral features



## Single wavelength LIF thermometry - NO - collisional case

#### Fixed laser wavelength

Simultaneous absorption by R22(2.5) and P22 (13.5)

transitions of NO- $\gamma$  (0,0) band



**RET effect** 





LIF OH Abs



## Single wavelength LIF thermometry - NO - collisional case

## $\kappa_{RET}/K_Q$

number of RET collisons within the lifetime as a function of air pressure

#### **RET effect**

increase pressure to 0.4 Torr





LIF OH Abs



## Single wavelength LIF thermometry - NO - collisional case

## $\kappa_{RET}/K_Q$

number of RET collisons within the lifetime as a func-

tion of air pressure



#### RET dependence on J

S. Lee, J. Luque, J. Reppel, A. Brown and D. Crosley

1378 J. Chem. Phys., Vol. 121, No. 3, 15 July 2004

TABLE III. Rate coefficients of the RET of the NO A  $^2\Sigma^+v'$  = 0 (10<sup>-11</sup> cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup>) in the Q<sub>1</sub>+P<sub>21</sub> band head with different colliders.

| $J_f$ | $N_2$  | O <sub>2</sub> | $N_2/O_2$ (79.5:20.5) | $N_2 \times 79.5 + O_2 \times 20.5$ |
|-------|--------|----------------|-----------------------|-------------------------------------|
| 4.5   | 8.30   | 6.50           | 7.22                  | 7.93                                |
| 5.5   | 5.05   | 4.61           | 4.76                  | 4.96                                |
| 6.5   | 3.93   | 3.27           | 3.43                  | 3.79                                |
| 7.5   | 2.52   | 2.19           | 2.31                  | 2.45                                |
| 8.5   | 1.90   | 1.69           | 1.84                  | 1.86                                |
| 9.5   | 1.51   | 1.20           | 1.24                  | 1.45                                |
| 10.5  | 1.14   | 0.91           | 1.01                  | 1.09                                |
| Kobs  | 28.6±3 | 17.4±2         | 25.0±3                | 26.3                                |

LIF OH Abs



### excitation spectrum LIF thermometry: excitation spectrum



#### Measurements of temperature and hydroxyl radical generation/decay in lean fuel-air mixtures excited by a repetitively pulsed nanosecond discharge



#### Zhiyao Yin<sup>a,\*</sup>, Aaron Montello<sup>a</sup>, Campbell D. Carter<sup>b</sup>, Walter R. Lempert<sup>a</sup>, Igor V. Adamovich<sup>a</sup>

<sup>3</sup> Michael A. Chaszeyka Nonequilibrium Thermodynamics Laboratories, Department of Mechanical Engineering, The Ohio State University, Columbus, OH 43210, United States <sup>b</sup> Air Force Research Laboratory, Wright-Patterson AFB, OH 45433, United States

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#### ABSTRACT

OH Laser Induced Fluorescence (LIF) and picosecond (ps), broadband Coherent Anti-Stokes Raman Spectroscopy (CARS) are used for time-resolved temperature and time-resolved, absolute OH number density measurements in lean H<sub>2</sub>-air, (CH<sub>2</sub>-air, Cd<sub>2</sub>+air, and Cd<sub>3</sub>H<sub>2</sub>-air mixtures in a nanosecond (ns) pulse discharge cell/plasma flow reactor. The premixed fuel-air flow in the reactor, initially at T<sub>0</sub> = 500 K and P = 100 torr, is excited by a repetitive ns pulse discharge in a plane-to-plane geometry (peak voltage 28 kV, discharge gap 10 mm, estimated pulse energy 1.25 mJ(pulse), operated in bust: mode at 10 kHz



LIF N<sub>2</sub>(A)

## Safe LIF thermometry: excitation spectrum

linear laser absorption regime

or partial saturation if absorption coefficients are similar

check that the quantum yield is the same for each rotational line excitation could be different with strong variations of the gas mixture composition



LIF N<sub>2</sub>(A)

## Safe LIF thermometry: excitation spectrum

linear laser absorption regime

or partial saturation if absorption coefficients are similar

check that the quantum yield is the same for each rotational line excitation could be different with strong variations of the gas mixture composition



Fig. 7. Typical OH LIF excitation spectrum used for temperature measurements. Spectrum taken 2 µs after the last pulse in the burst (v = 10 kHz, 50 pulses). H<sub>2</sub>-air, T<sub>0</sub> = 500 K, P = 100 torr, \phi = 0.12.



## When electronic quenching is a problem: LIF detection of $N_2(A^3\Sigma_u^+)$ metastable

## Choose a strong enemy, he will make you grow up to face him

indio proverb



# Optical-Optical Double Resonance (OODR) LIF detection of $N_2(A^3\Sigma_u^+)$ metastable

classical single-photon absorption

 $N_2(A^3\Sigma^+_u) + h\nu_l 
ightarrow N_2(B^3\Pi_g)$ 

fluorescence

 $N_2(B^3\Pi_g) 
ightarrow N_2(A^3\Sigma^+_u) + h\nu_f$ 





LIF thermometry

# Optical-Optical Double Resonance (OODR) LIF detection of $N_2(A^3\Sigma_u^+)$ metastable

classical single-photon absorption

 $N_2(A^3\Sigma^+_u) + h\nu_l 
ightarrow N_2(B^3\Pi_g)$ 

fluorescence

$$N_2(B^3\Pi_g) 
ightarrow N_2(A^3\Sigma^+_u) + h 
u_f$$

#### the quantum yield is low

$$Y = rac{A_{v',v''}}{A_{v'} + \sum_i k_i [Q_i]} pprox 10^{-4}$$
  
at ATP in N<sub>2</sub>



LIF thermometry  $(LIF N_2(A))$ 

# Optical-Optical Double Resonance (OODR) LIF detection of $N_2(A^3\Sigma_{\mu}^+)$ metastable

two resonant photons absorption

$$\begin{split} & N_2(A^3\Sigma_u^+) \ + \ h\nu_{l1} \ \rightarrow \ N_2(B^3\Pi_g) \ + \\ & h\nu_{l2} \ \rightarrow \ N_2(C^3\Pi_u) \end{split}$$

#### fluorescence

 $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu_f$ 





# Optical-Optical Double Resonance (OODR) LIF detection of $N_2(A^3\Sigma_u^+)$ metastable

two resonant photons absorption

$$\begin{split} & N_2(A^3\Sigma_u^+) \ + \ h\nu_{l1} \ \rightarrow \ N_2(B^3\Pi_g) \ + \\ & h\nu_{l2} \ \rightarrow \ N_2(C^3\Pi_u) \end{split}$$

#### fluorescence

$$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu_f$$

the quantum yield is two orders of magnitude larger

$$Y = \frac{A_{v',v''}}{A_{v'} + \sum_{i} k_i[Q_i]} \approx 10^{-2}$$
  
at ATP in N<sub>2</sub>











LIF OH /







LIF thermometry







LIF thermometry

# Optical-Optical Double Resonance (OODR) LIF detection of $N_2(A^3\Sigma_{\mu}^+)$ metastable

simultaneous lasers firing within 1 ns for max. signal at p=1 atm.

step 1: Nd-YAG pumped dye  $\lambda \sim 680 nm$ 

step 2: Nd-YAG pumped dye + SHG by BBO crystal  $\lambda \sim 350$  nm



LIF thermometry

## OODR-LIF detection of $N_2(A^3\Sigma_u^+)$ - excitation spectra

### N<sub>2</sub>(B-A) transition

excitation: (3,0) band - detection (3,1) band

## N<sub>2</sub>(C-B) transition

excitation: (2,3) band - detection (2,1) band



### For maximum signal and $T_{rot}$ independence (for $T_{rot} < 400K$ )

 $\lambda_1$  excites  $P_{11}, \, Q_{12}$  heads - J'' = 1 - 10

 $\lambda_2$  tuned to J = 10 - 15 of the  $P_{11}$  branch



LIF OH

## Calibration of OODR-LIF

 $\frac{N_2(A^3\Sigma_u^+) \text{ by OODR-LIF}}{NO-\gamma \text{ emission}}$   $\frac{N_2(A^3\Sigma_u^+) + NO(X) \rightarrow NO(A^2\Sigma^+) + N_2(X)}{NO(A^2\Sigma^+) + N_2(X)}$ 



LIF thermometry





## Calibrated OODR-LIF $N_2(A^3\Sigma_u^+)$ density in a diffuse discharge (APTD)

#### our result

N<sub>2</sub> APTD at 1.8 KHz

#### calculations

F. Massines et al. 2005 Plasma Phys.

Control. Fusion 47 B577





LIF thermometry



# $N_2({\cal A}^3\Sigma_u^+)$ density in $N_2$ plus small $O_2$ admixtures: the transition from diffuse to filamentary regime

time-resolved LIF

The metastable density remains large through the transition





# $N_2(A^3\Sigma_u^+)$ density in $N_2$ plus small $O_2$ admixtures: the transition from diffuse to filamentary regime

#### time-resolved LIF

The metastable density remains large through the transition



### N<sub>2</sub>(A) quenching

#### remarkably increases at the transition

LIF thermometry





## Alternative single-laser OODR-LIF schemes

| laser system           | $\lambda_1 + mix(\lambda_1, \lambda_2)$ | Ti-Sa + TH        | Nd-YLF + Dye/OPO         |  |  |  |
|------------------------|---|-------------------|--------------------------|--|--|--|
| FPS band               | (3,0)                                   | (1,0)             | (0,0)                    |  |  |  |
| $\lambda$ bandhead (Å) | 6875.24                                 | 8919.39           | 10510.04                 |  |  |  |
| $A_{ij}(s^{-1})$       | $1.07	imes10^4$                         | $8.72 	imes 10^4$ | $6.25	imes10^4$          |  |  |  |
| SPS band               | (2,3)                                   | (3,1)             | $\Delta v = -1, 0, 1, 2$ |  |  |  |
| $\lambda$ bandhead (Å) | 3500.5                                  | 2962.0            | 2814.3 - 3567.9          |  |  |  |
| $A_{ij}(s^{-1})$       | $1.65	imes10^{6}$                       | $8.68	imes10^{6}$ |                          |  |  |  |
|                        |   |                   |                          |  |  |  |

Nd-YLF (Yttrium-Lithium-Fluoride)  $\lambda = 1047 - 1053$  nm



#### LIF for analytical purposes is basically an absorption experiment

but with a different observable: emission from an excited electronic state



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- byproduct: measurement of collision rate constant by selective v-level excitation



## Concluding remarks

And what does all this equal to, in terms of people? Does it suggest that man and human knowledge are fallible: that theories are works of art, however criticizable objectively, and as a result this fact makes it possible for us to progress, progress in an objective way; that all of us contribute to constructing objective knowledge, as artisans who construct a cathedral; and all this becomes a part of life's adventure.

Karl Popper, March 1970





## **Concluding remarks**

If I am stronger it's because I have in me not my little life only but all the lives and I go on securely because I have thousands of eyes

Pablo Neruda
Introduction





