# Spectroscopic Challenges in the Modeling of High Temperature Air Plasma Radiation for Aerospace Applications

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# Aerospace Applications

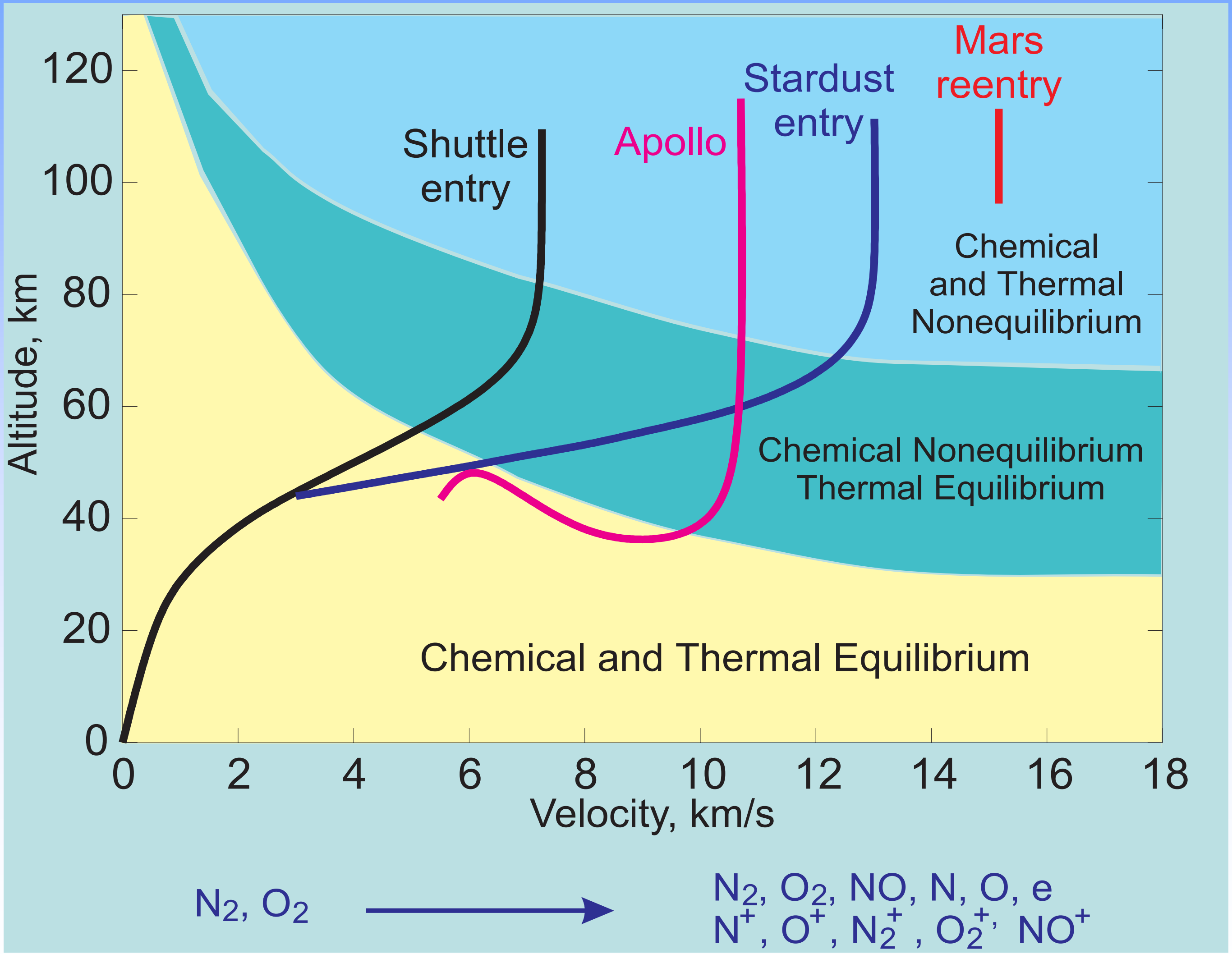
- Increasing number of space missions:
  - Moon (Orion): air
  - Titan (Cassini-Huygens): $N_2/CH_4$
  - Mars: air or $N_2/CO_2$
  - Comets (Stardust): air
  - Jupiter: H, He

- Increasing number of ground-based diagnostic facilities with high resolution capabilities

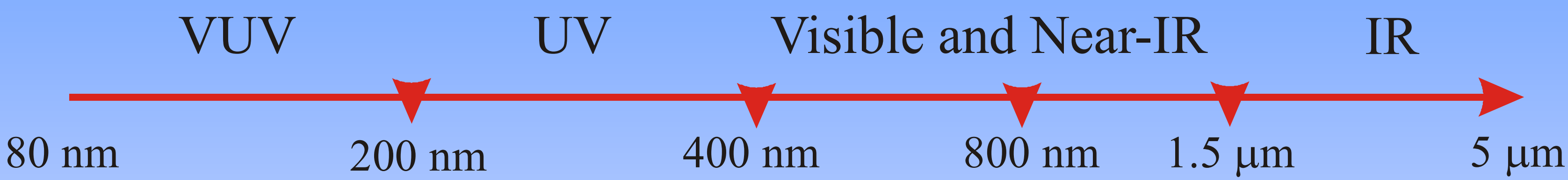
- Spectroscopic data needed to:
  - estimate radiative heat fluxes
  - characterize thermochemical state of plasma (in flight or ground based)

- Needs:
  - term energies for high-lying rotational levels (J up to 100)
  - transition probabilities
  - lineshapes (in particular predissociation linewidths)
  - state-to-state collision cross-sections (heavy-heavy, electron-heavy)

# Nonequilibrium Regimes in Atmospheric Reentry



# Radiative Transitions in Atmospheric Reentry Plasmas




$N_2$ Birge-Hopfield 2
$N_2$ Birge-Hopfield 1
$N_2$ Worley-Jenkins
$N_2$ Worley
$N_2$ Carroll-Yoshino
$N_2$ e'-X
CO (4+)

$O_2$ Schumann-Runge
$N_2^+$ First Negative
$N_2$ First Positive
$N_2$ Second Positive
CN Violet
NO $\beta$
NO $\gamma$
NO $\delta$
NO $\varepsilon$
NO $\beta'$
NO $\gamma'$
OH A-X
NH A-X

$C_2$ Swan
CN Red
$N_2^+$ Meinel

NO C-A
NO D-A
NO F-C
NO E-C
NO E-D
NO H-C
NO H-D
NO H'-C
NO H'-D

NO X-X
$NO^+$ X-X
CO X-X
OH X-X

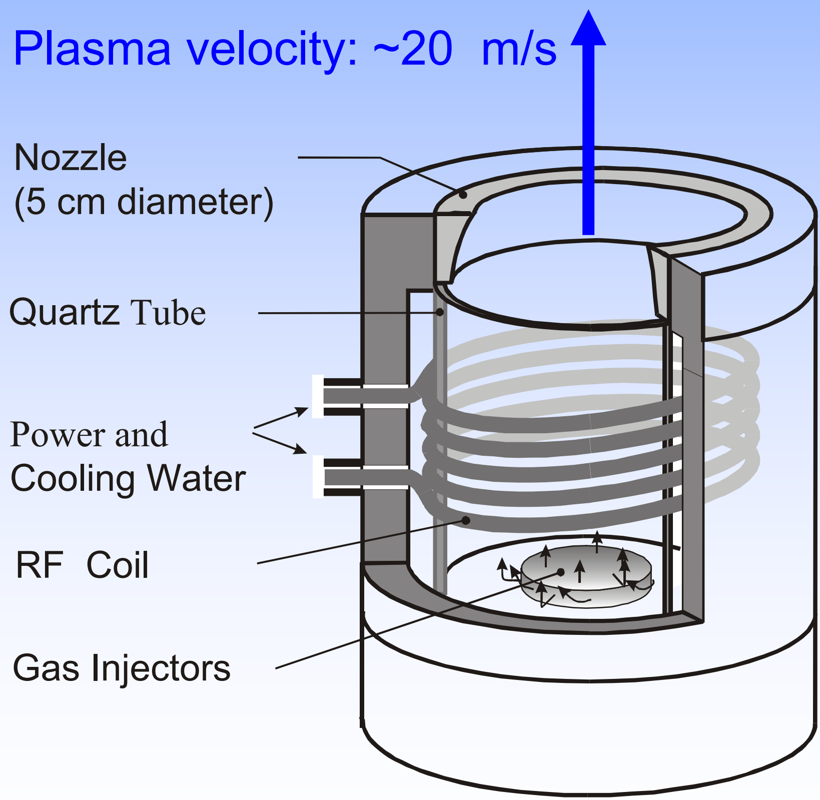
N: 1484 lines (86.523 nm to 54.83 µm)
O: 856 lines (69.753 nm to 16.71 µm)
C: 1291 lines (94.519 nm to 12.28 µm)

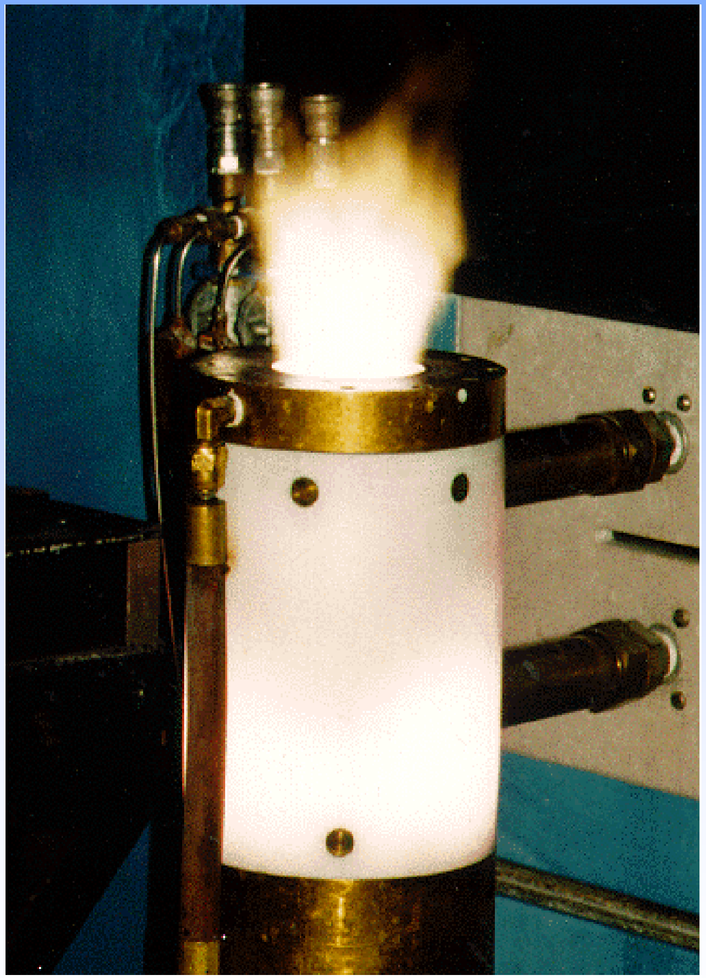
# Contents

- Spectroscopic models and validation experiments
  - 200-800 nm
  - 80-200 nm
  - 800-5.5 μm
- Predissociation

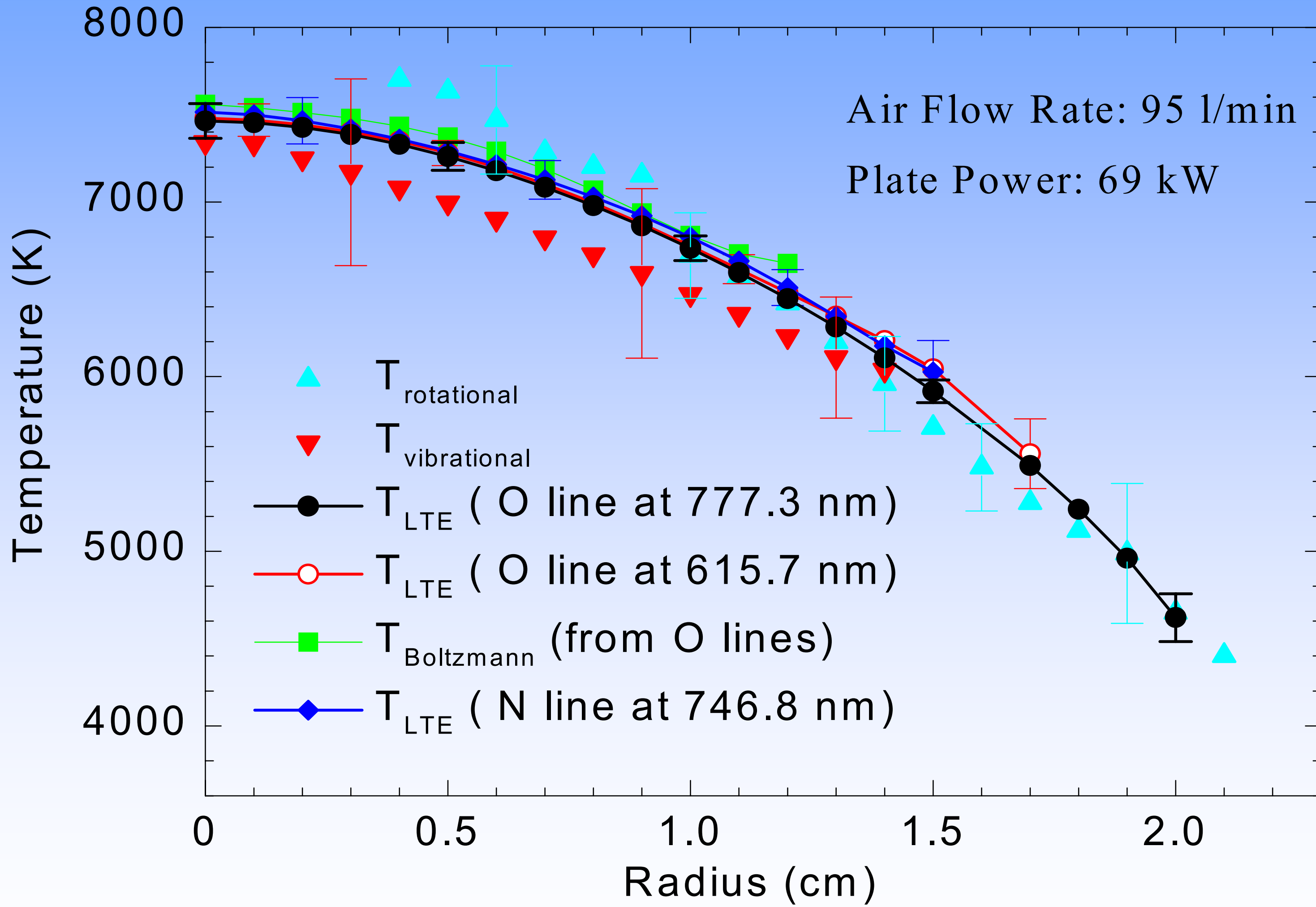
# Measurements and modeling of air plasma radiation between 185 and 800 nm

# Generation of LTE Air Plasmas:
# 50 kW radio-frequency inductively coupled plasma torch



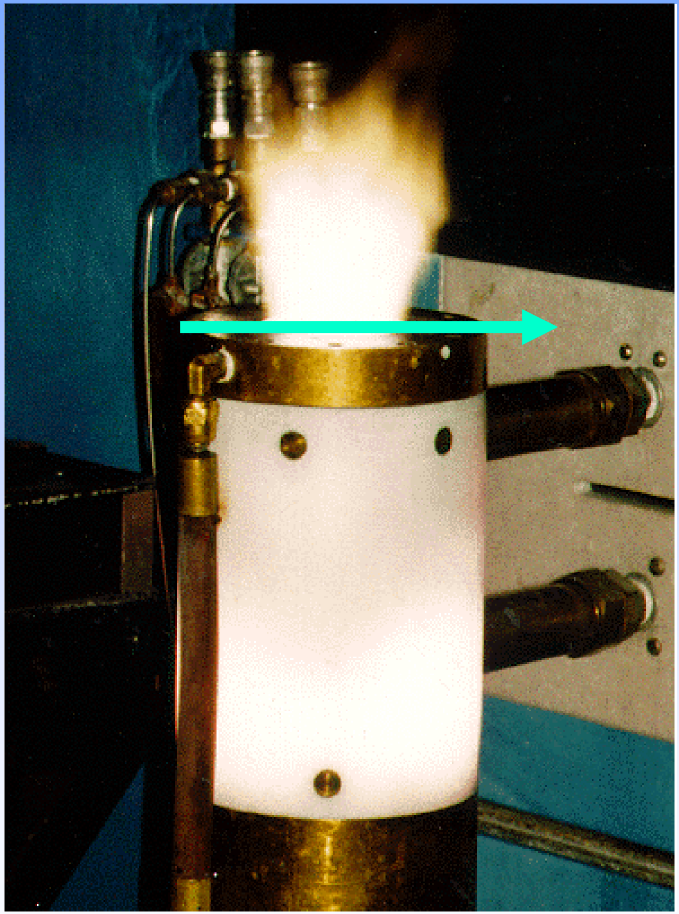



# Temperature Measurements at Torch Exit



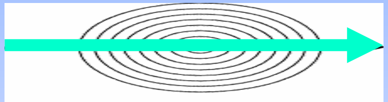

- Plasma is in LTE

# Measured and Predicted LTE Emission Spectra



SPECAIR Radiation Code

(www.specair-radiation.net)



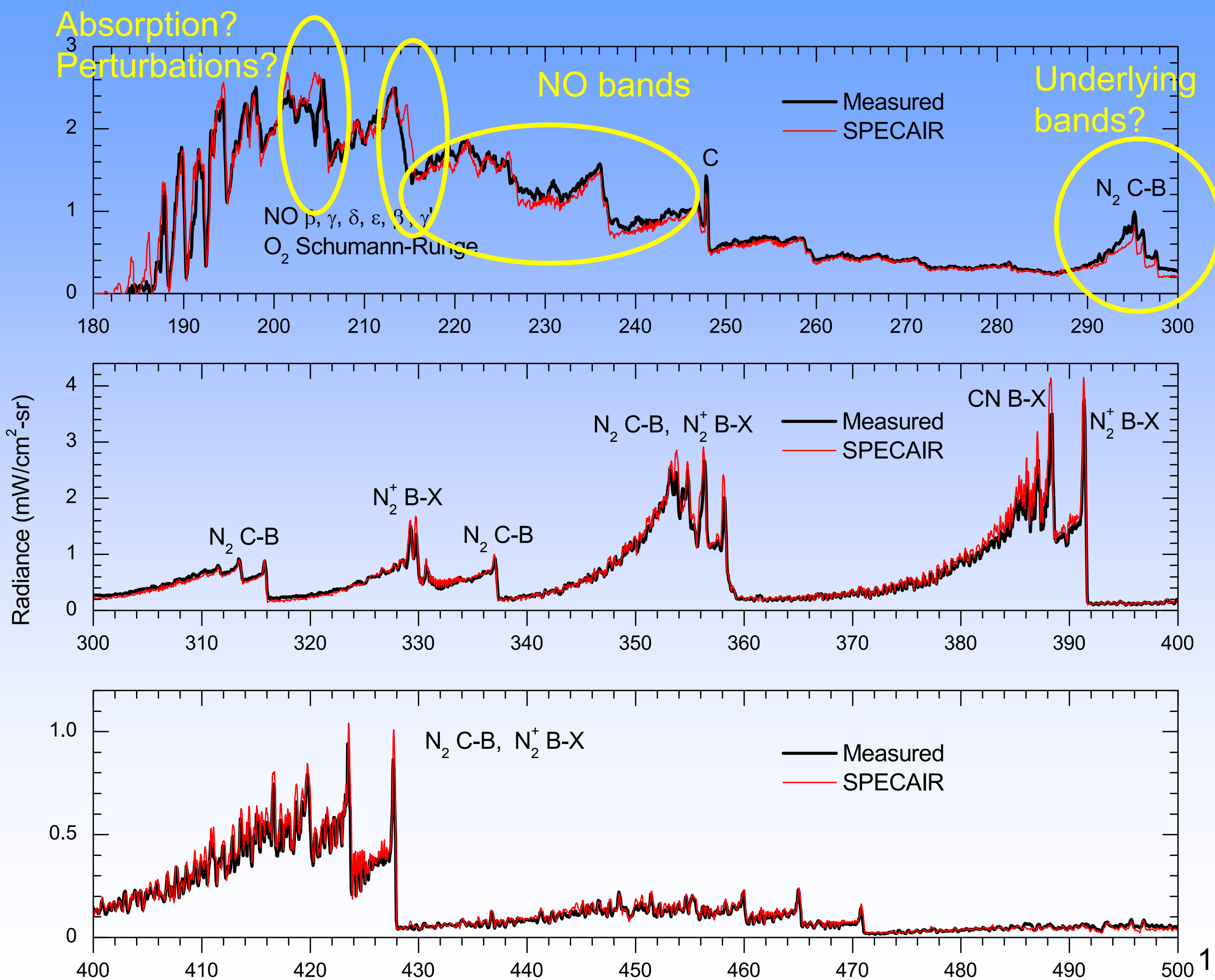
- Calculate emission spectrum using measured temperature and equilibrium concentrations
- Solve radiative transport equation
- Convolve with slit function
- Compare with calibrated experimental spectrum

# SPECAIR Model

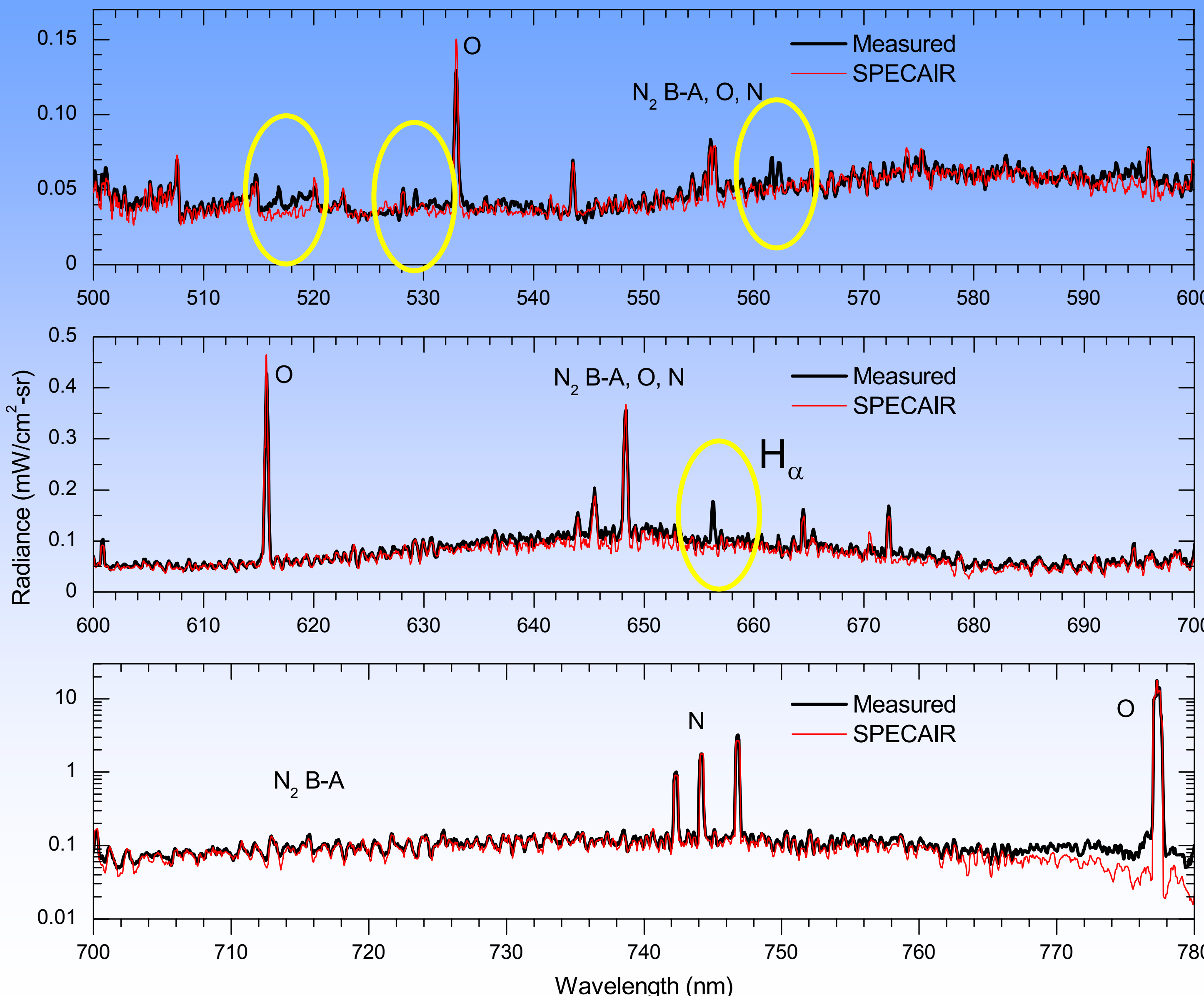
- Transition Probabilities:
  - Electronic-vibrational transition moments calculated using *ab initio* ETMFs
  - Hönl-London factors obtained with HONL program of Whiting

- Line positions:
  - $N_2$ VUV systems: Coupled 30x30 hamiltonian matrix for b,c,o states; 40x40 matrix for b',c',e' (Stahel et al., *JCP* 1983)
  - NO UV/VUV systems: Coupled 138x138 hamiltonian for B,C,L,K,Q (Gallusser and Dressler, *JCP* 1982)
  - $N_2^+$: Coupled 13x13 hamiltonian for B state (Michaud *et al*, *JMS* 2000)
  - $N_2$ 1+, 2+: Hamiltonians of Roux *et al*. (*JMS* 1983 & 1993, *CJP* 1989 &1990)
  - OH: Hamiltonian of Stark, Brault, Abrams (*Opt. Soc. Am.,* 1994)
  - Atomic lines: NIST ASD database

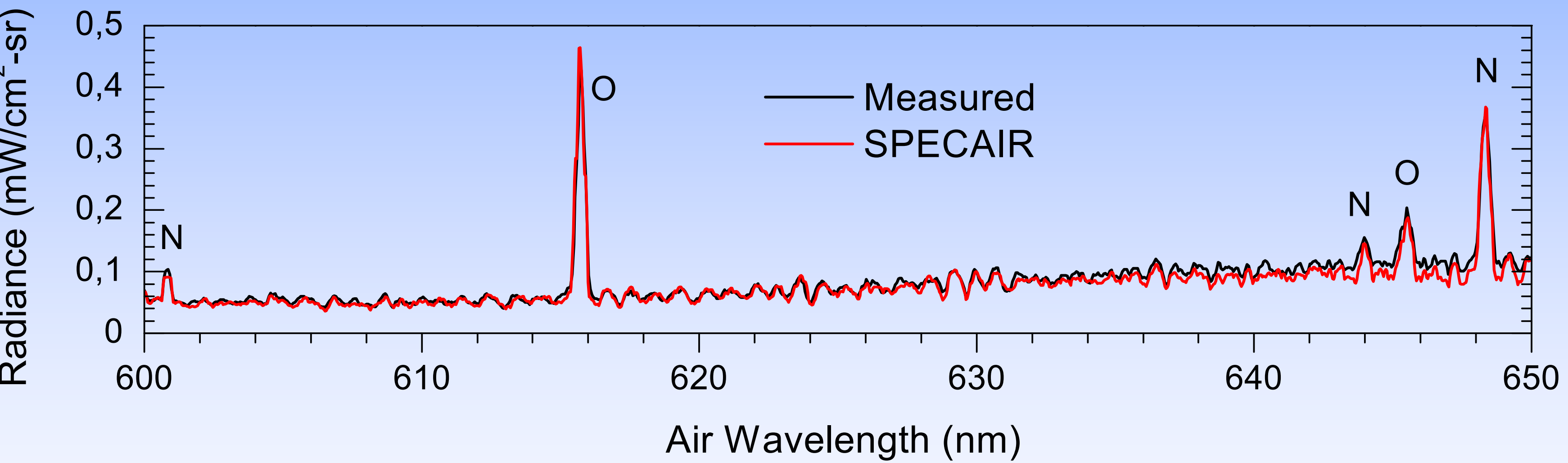
# Measured and SPECAIR Emission in LTE Air:  185-500 nm



# Measured and SPECAIR Emission in LTE Air:  500-800 nm



# Emission in LTE Air:  600-650 nm

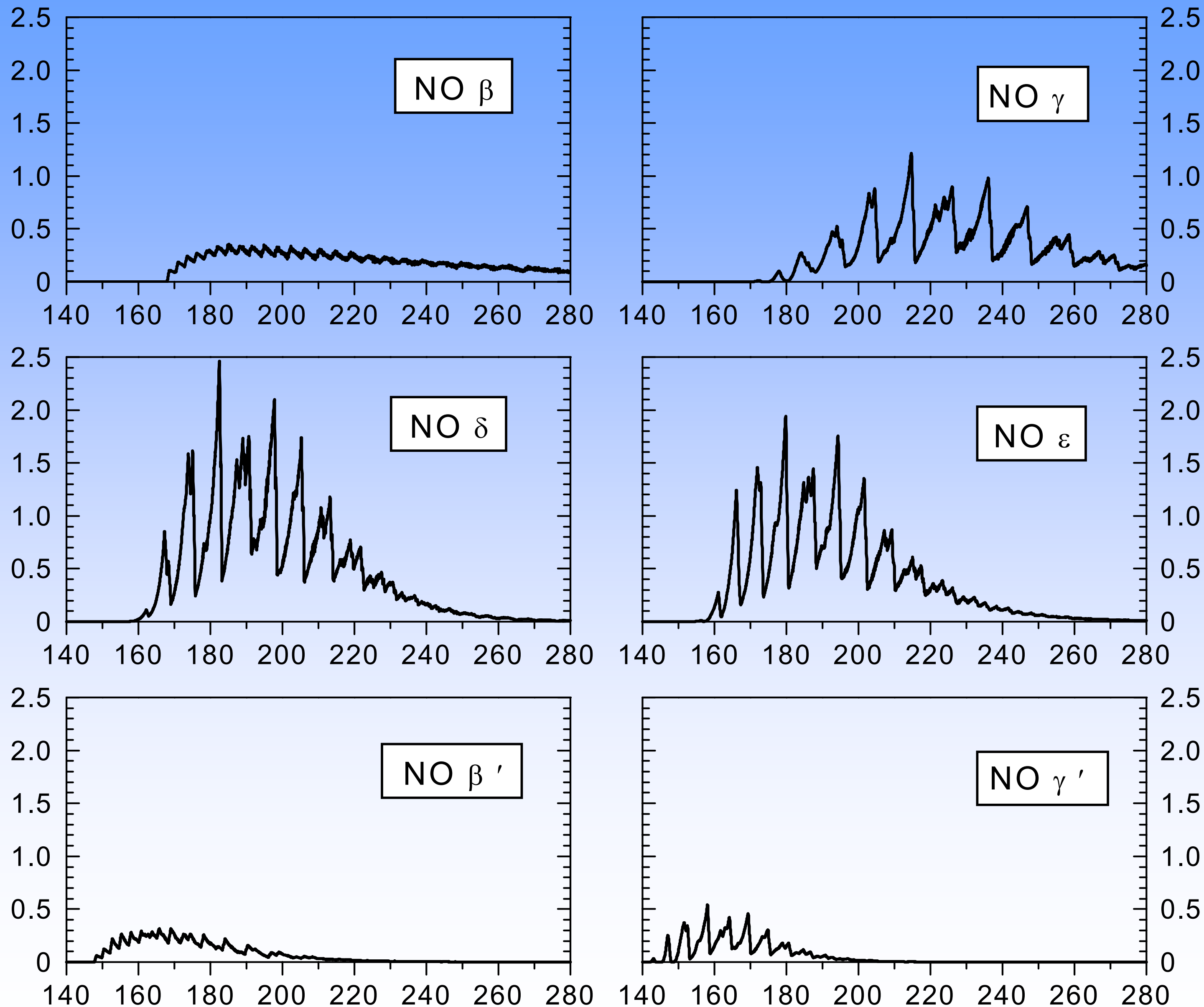


# Measurements and modeling of air plasma radiation between 80 and 200 nm

- VUV radiation:
  - self-absorbed, or absorbed by Schumann Runge continuum.
  - important radiative heat transfer mechanism

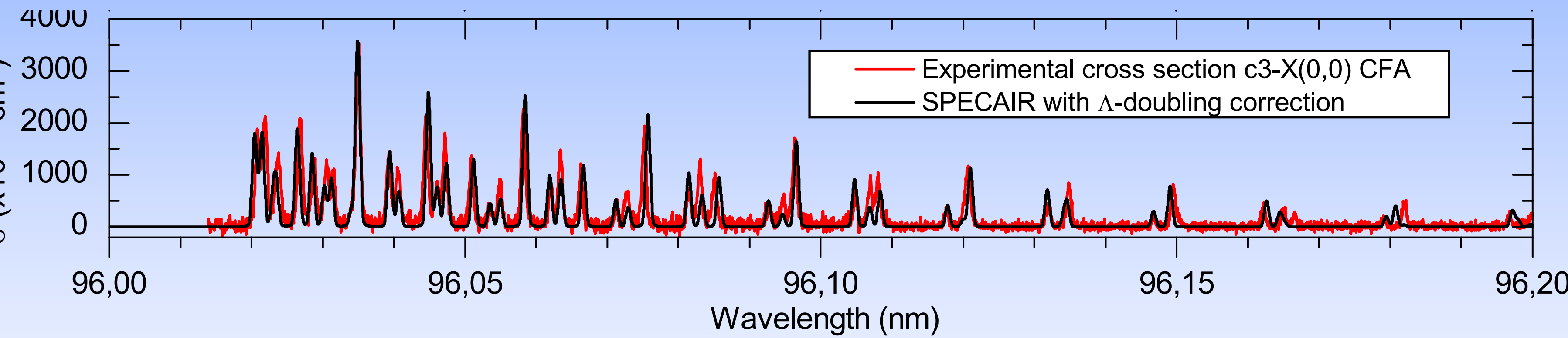
- Sources of VUV radiation in air:
  - **atomic lines of O, N, C**: well in hand (ASD)
  - **NO transitions (A-X, B-X, C-X, D-X, B'-X, E-X, F-X,…):** modeled in SPECAIR, but no experimental validation below 200 nm
  - **$N_2$ transitions: $^1\Sigma$-$^1\Sigma$ ( b'-X, $c'_4$-X, e'-X) and $^1\Pi$-$^1\Sigma$ (b-X, $c_3$-X, $o_3$-X) :** SPECAIR model based on perturbed transition probabilities computed with coupled 30x30 hamiltonian matrix for b,c,o states and 40x40 matrix for b',c',e' (Stahel, Leoni, Dressler, *JCP* 1983)

# Predicted NO transitions in the range 140-280 nm



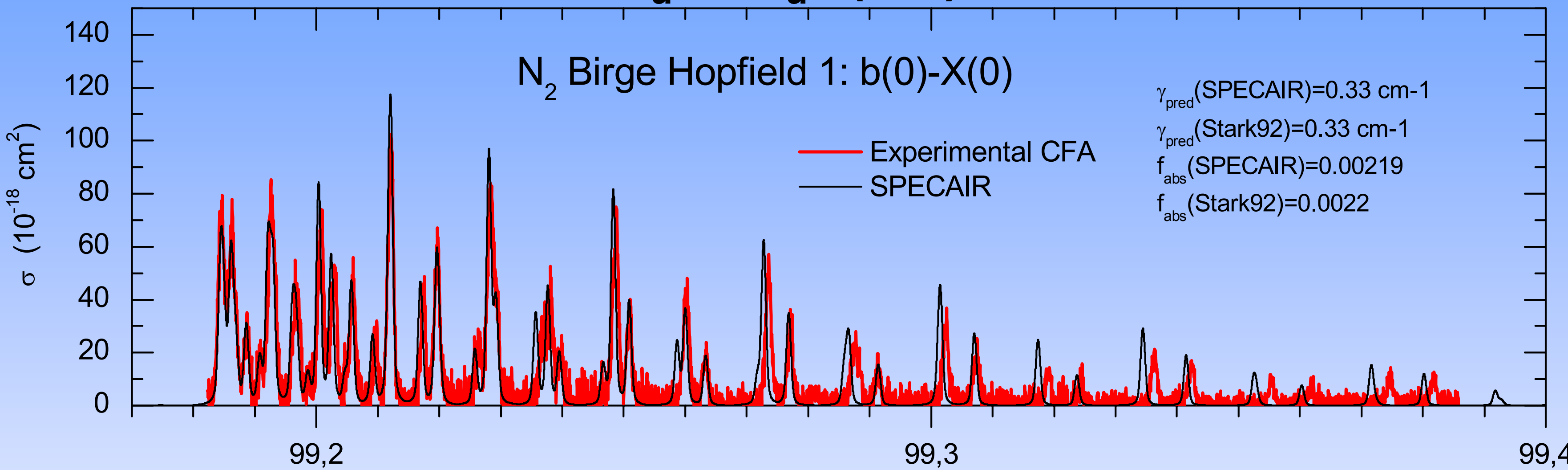
# $N_2$ EUV transitions: Comparison SPECAIR – CFA absorption cross sections (Stark, Smith, Huber, Yoshino, Stevens, Ito, *JCP* 1992)

## $c_3{}^1\Pi_u$-$X^1\Sigma_u^+$ (0,0)

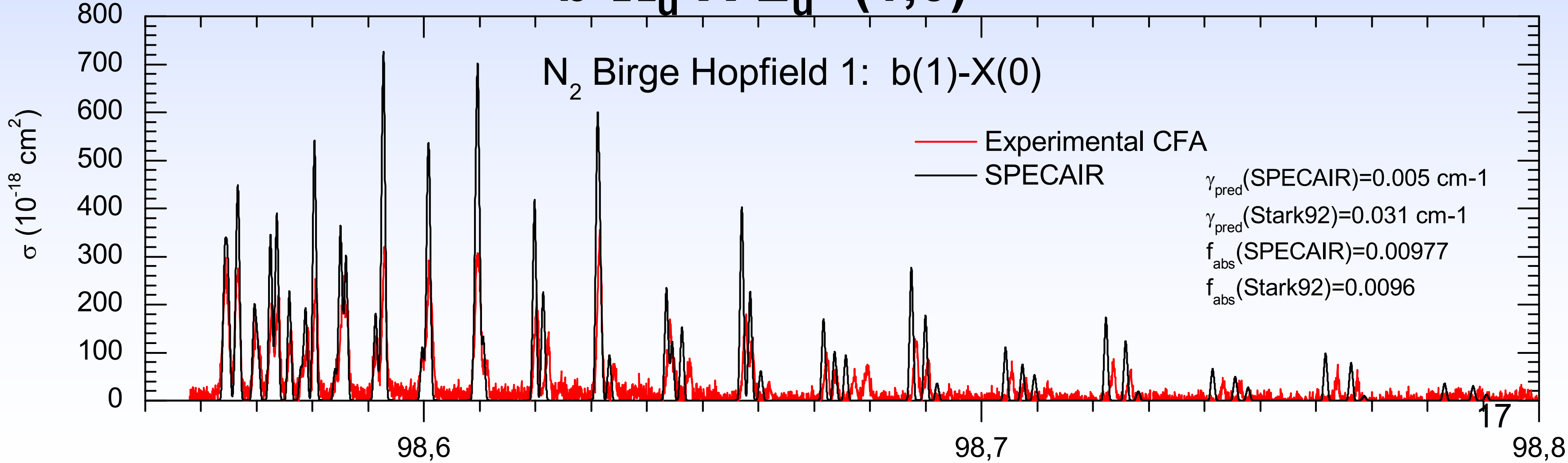


# Comparison SPECAIR – CFA absorption cross sections

## $b^1\Pi_u$-$X^1\Sigma_u^+$ (0,0)

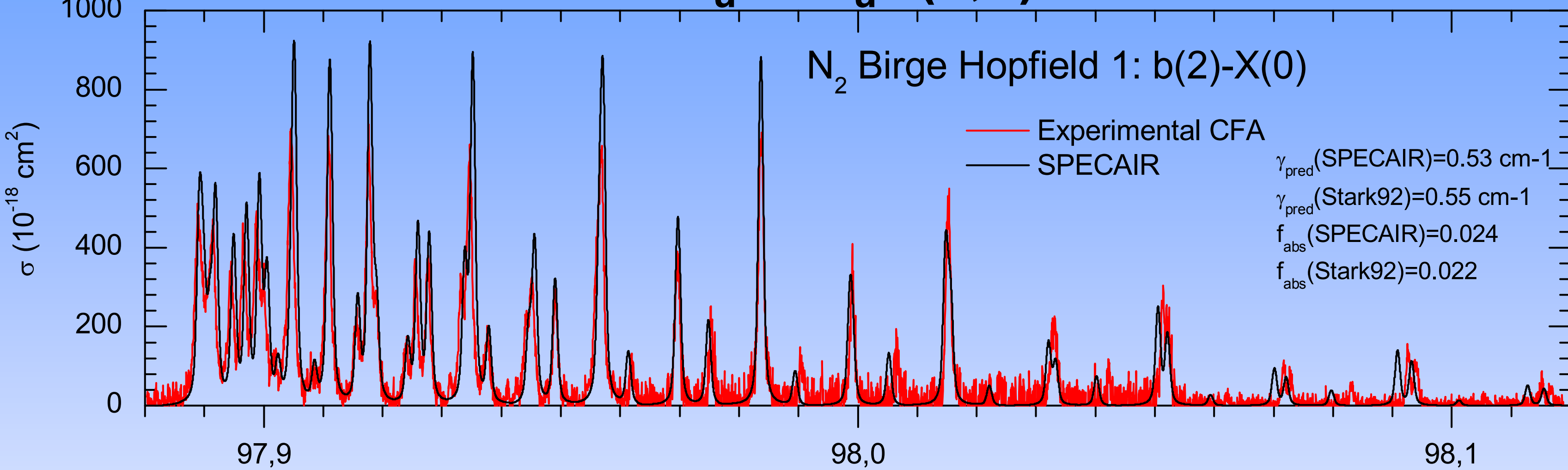



## $b^1\Pi_u$-$X^1\Sigma_u^+$ (1,0)

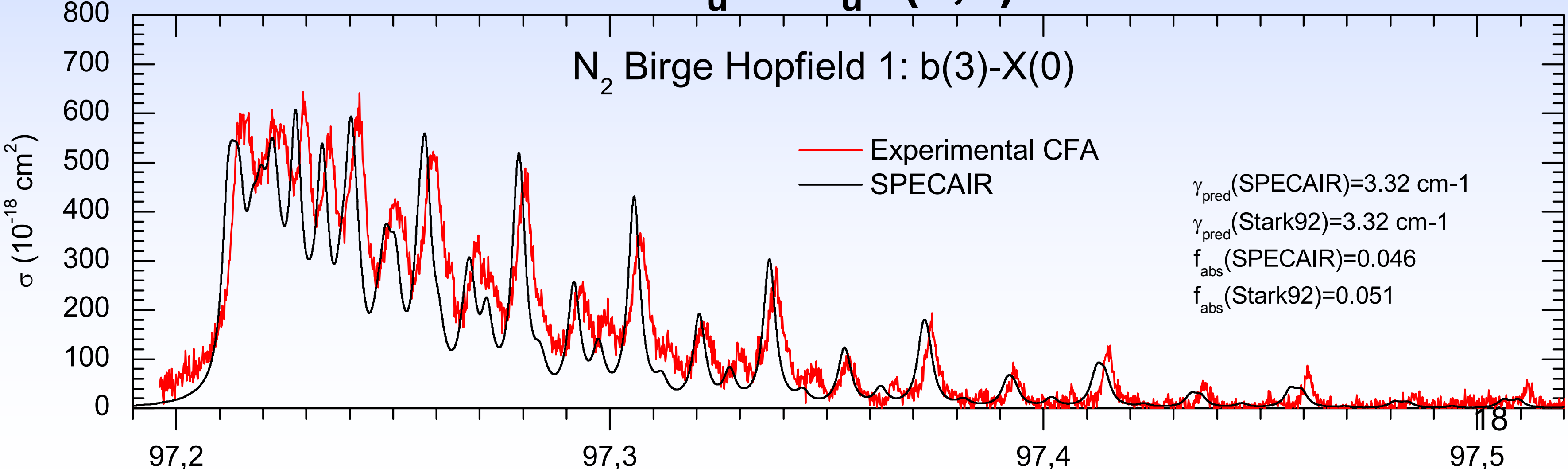


# Comparison SPECAIR – CFA absorption cross sections

## $b^1\Pi_u$-$X^1\Sigma_u^+$ (2,0)

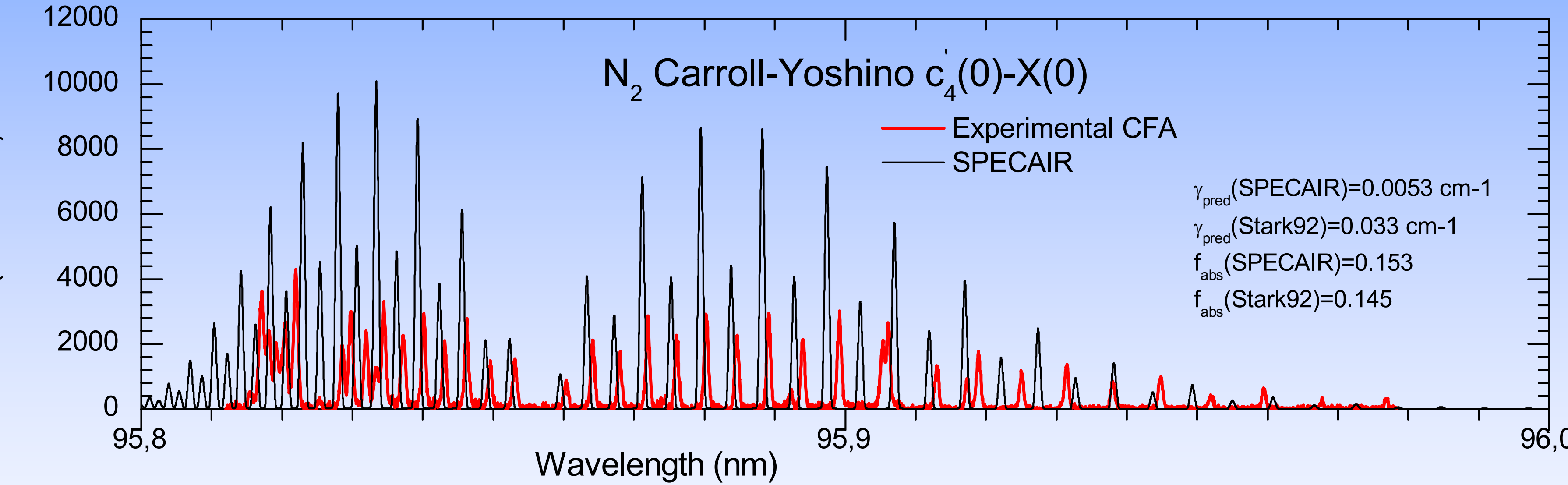



## $b^1\Pi_u$-$X^1\Sigma_u^+$ (3,0)



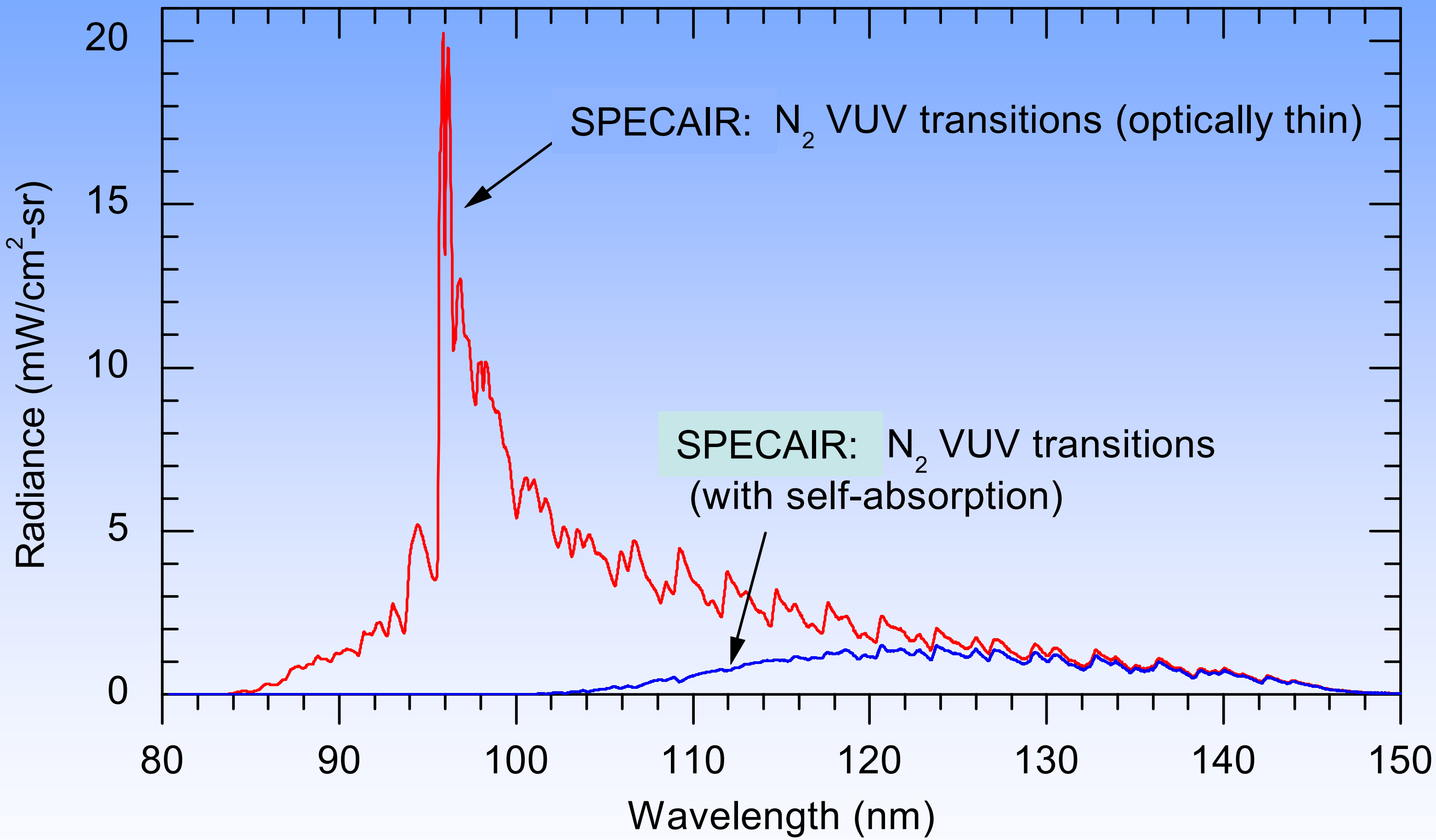
# Comparison SPECAIR – CFA absorption cross sections

**$c'_4{}^1\Sigma_u^+ - X^1\Sigma_u^+$ (0,0)**




Better agreement obtained with more recent CFA data of Stark et al. 2000, still not perfect

# $N_2$ VUV Band Systems for Plasma Torch Conditions

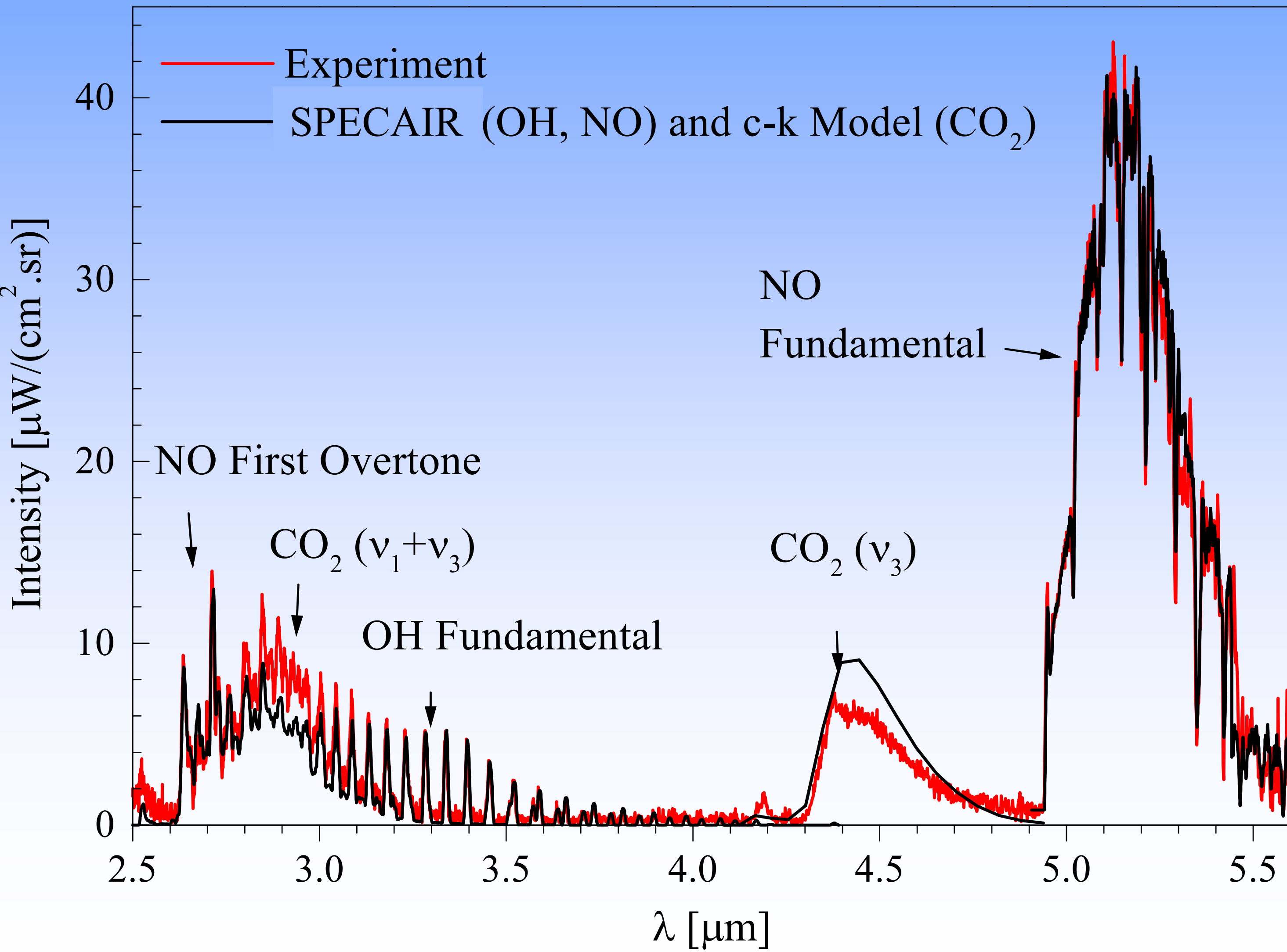



- Self-absorbed radiation affects temperature profile
- Part of Birge-Hopfield 1 and 2 radiation escapes from plasma

# Measurements and modeling of air plasma radiation between 800 nm and 5.5 micron

- Dominant systems:
  - 800 nm – 2.5 micron: NO C-A, D-A, E-C, E-D, F-C, H-C, H-D, …*(see Laux et al. AIAA Paper 95-2124, 1995)*
  - 2.5 – 5.5 micron: OH X-X, NO X-X, CO X-X, $CO_2$
- $NO^+$ X-X: importance for optical diagnostics

# Infrared Radiation of Air at ~3400 K: 2.5-5.5 micron



# Infrared bands of $NO^+$: Interest for optical diagnostics

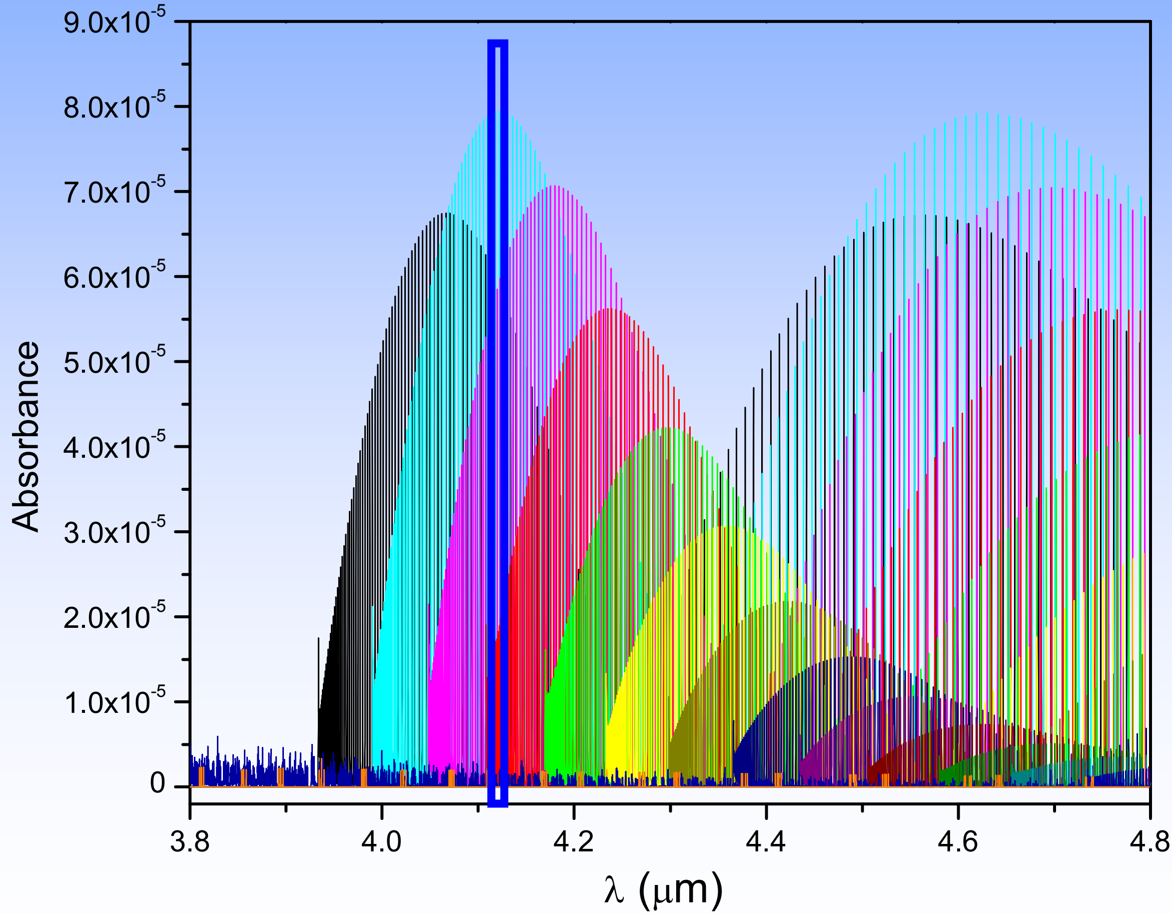
- Motivation: $NO^+$ is the dominant ion in atmospheric pressure air plasmas under a wide range of conditions

- Detection:
  - no electronic transitions readily accessible
  - rovibrational bands in the mid-IR (~4 micron range) require sensitive laser technique (e.g. Cavity Ring Down Spectroscopy)

    (Yalin, Laux, and Zare, in *Nonequilibrium Air Plasmas at Atmospheric Pressure*, Chapter 8. Diagnostics, pp. 531-535, 2005)

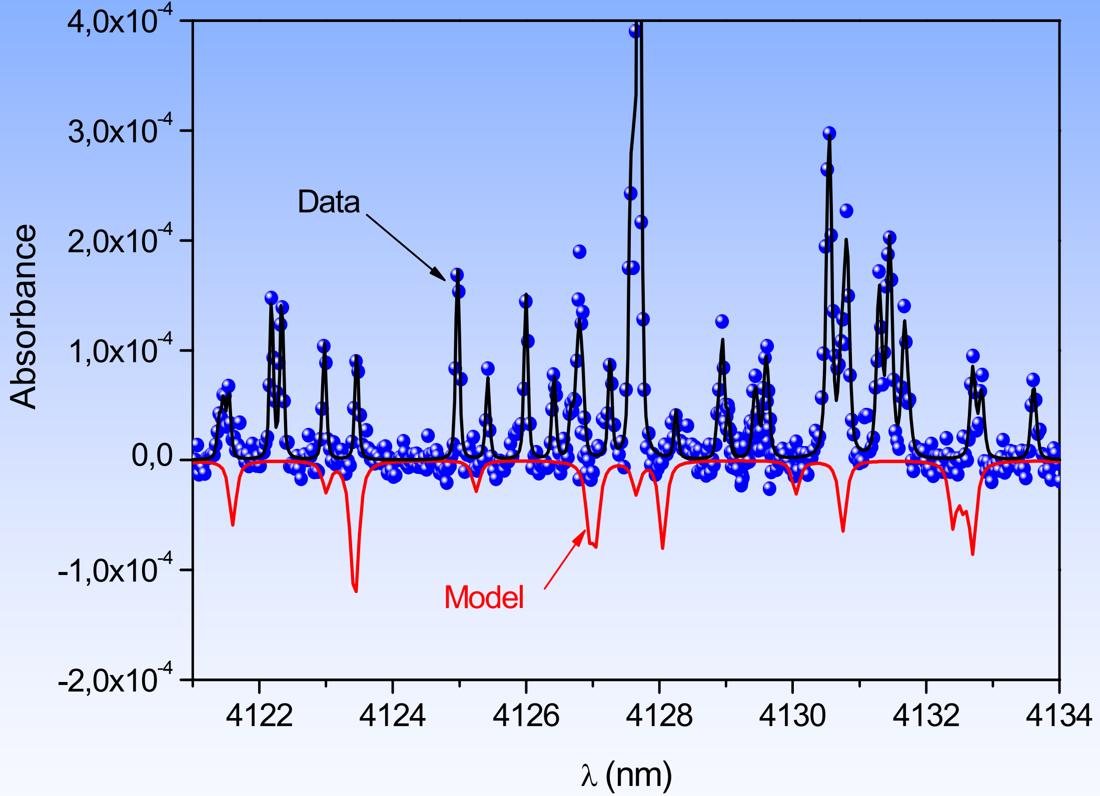
# Rotational lines of $NO^+$ (Cavity-Ring Down Spectroscopy)

SPECAIR model:
Line positions from Jarvis, Evans, Ng, and Mitsuke, JCP **111**(7), 3058-3069 (1999).
obtained from pulsed field ionization photoelectron measurements)



# Rotational lines of $NO^+$ (Cavity-Ring Down Spectroscopy)

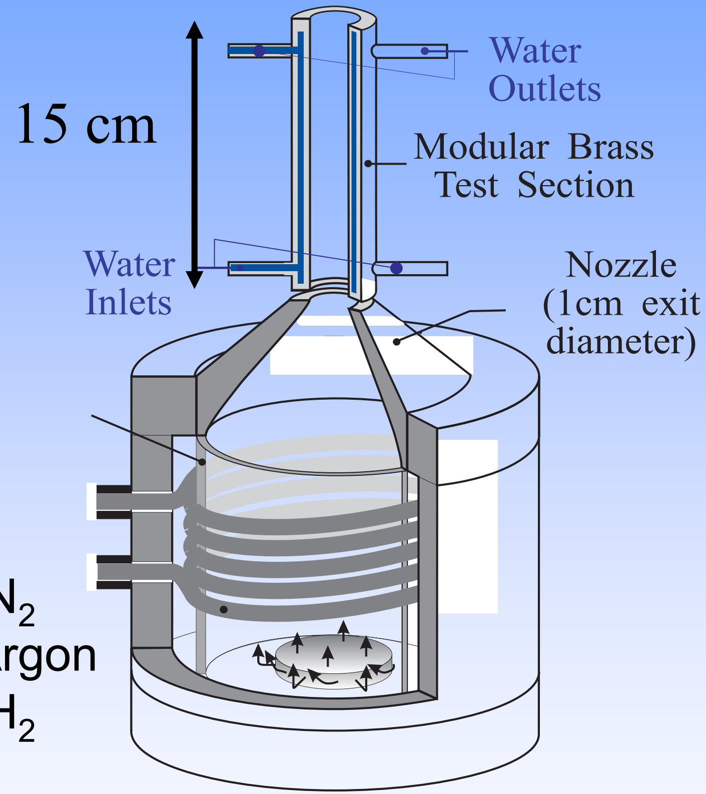
CRDS measurements in plasma torch (air)




Experimental $B_v$ has an uncertainty of +/- 0.005 $cm^{-1}$ (~ 0.25%) insufficient for interpretation of CRDS measurement

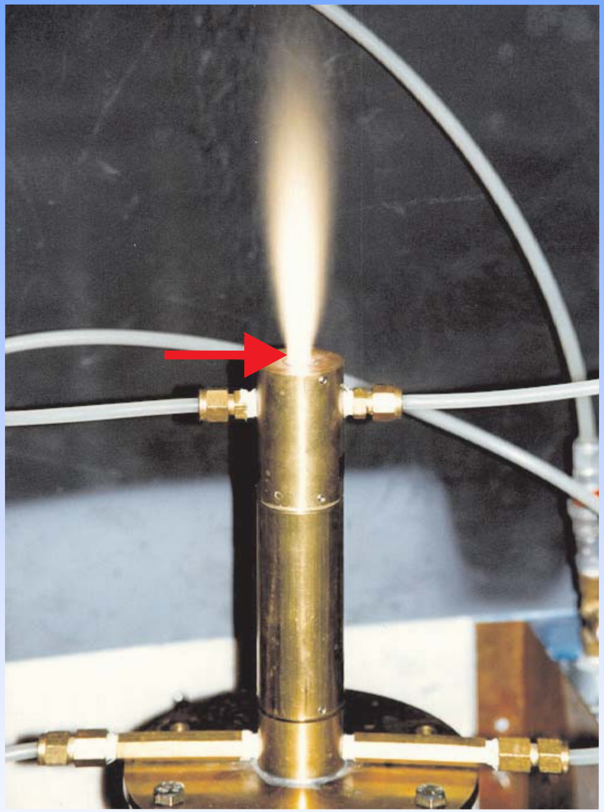
# Effect of predissociation on spectral emission

# Recombining Nitrogen Plasma



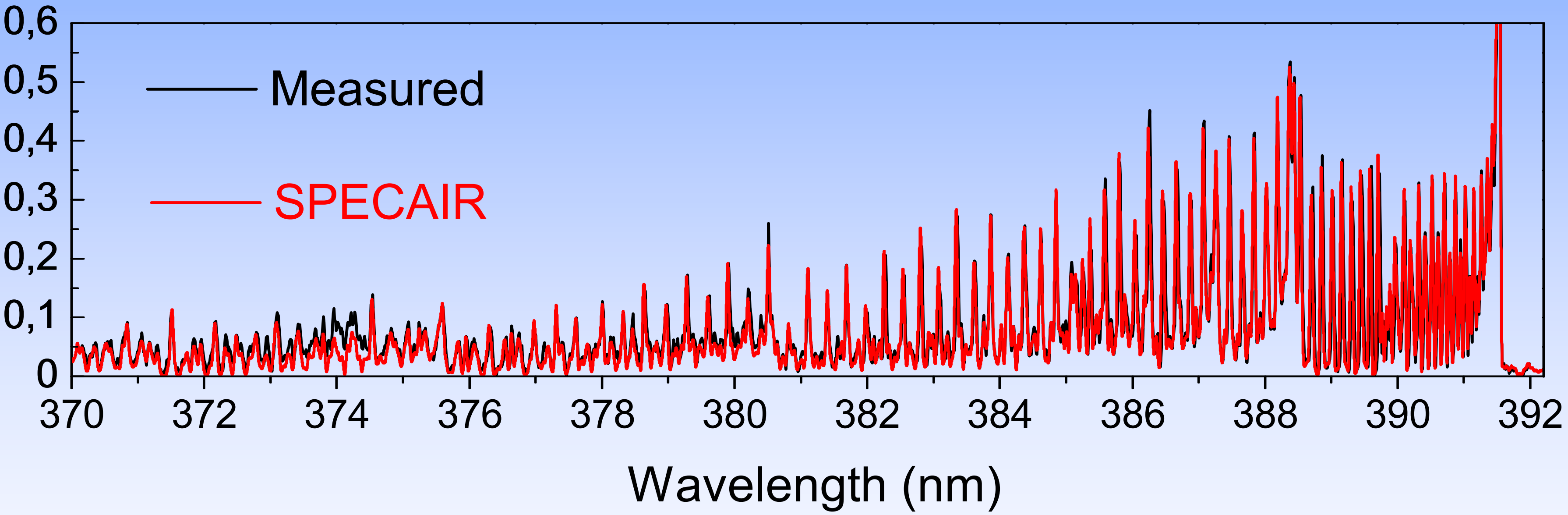

~ 1 km/s

100 slpm $N_2$
50 slpm Argon
2.3 slpm $H_2$



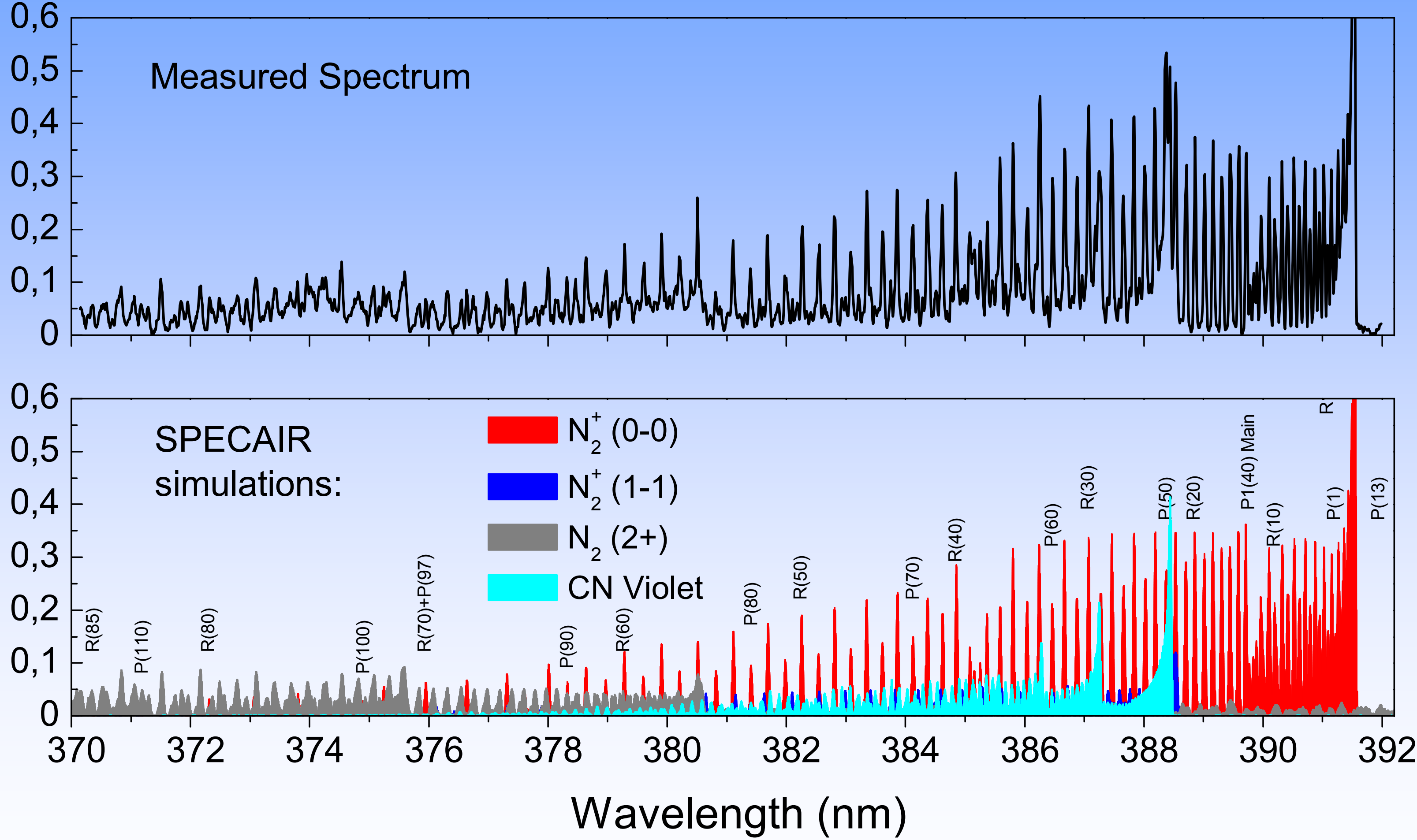
- Within the test-section, the temperature decreases from 7200 to 4850 K in 250 μs ⇒ nearly frozen N-atom conc.

# Rotational temperature at test-section exit using $N_2^+$



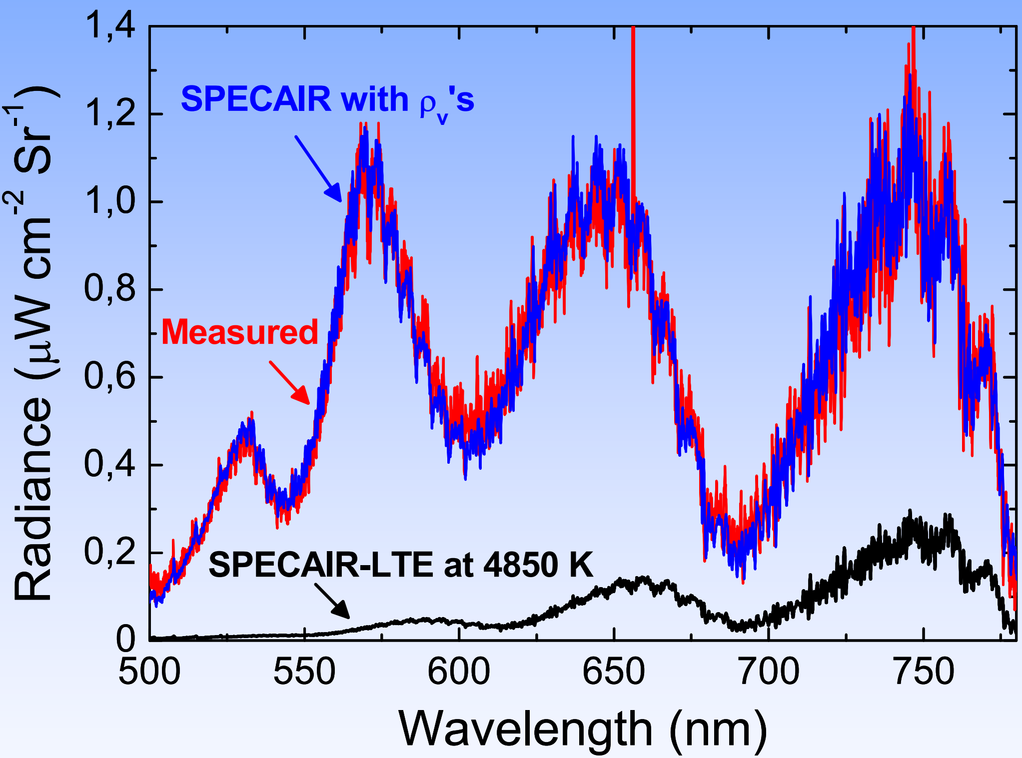

- Best fit: $T_{rot} = T_{vib} = 4850 \pm 100$ K

# Transitions from high *J*'s are critical

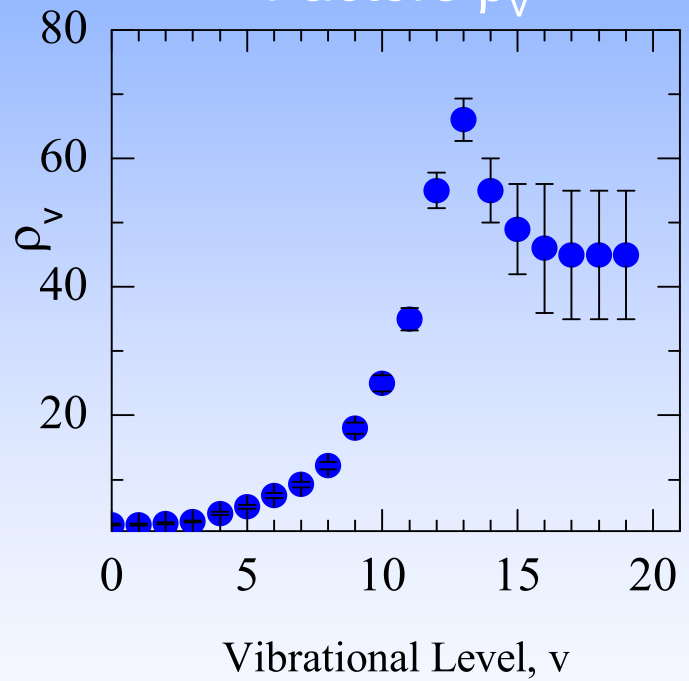



N2+: FTS work of Michaud, Roux, Davis (*JMS* 2000): J's up to 100

# Analysis of the $N_2$ B-A spectrum at exit of test-section



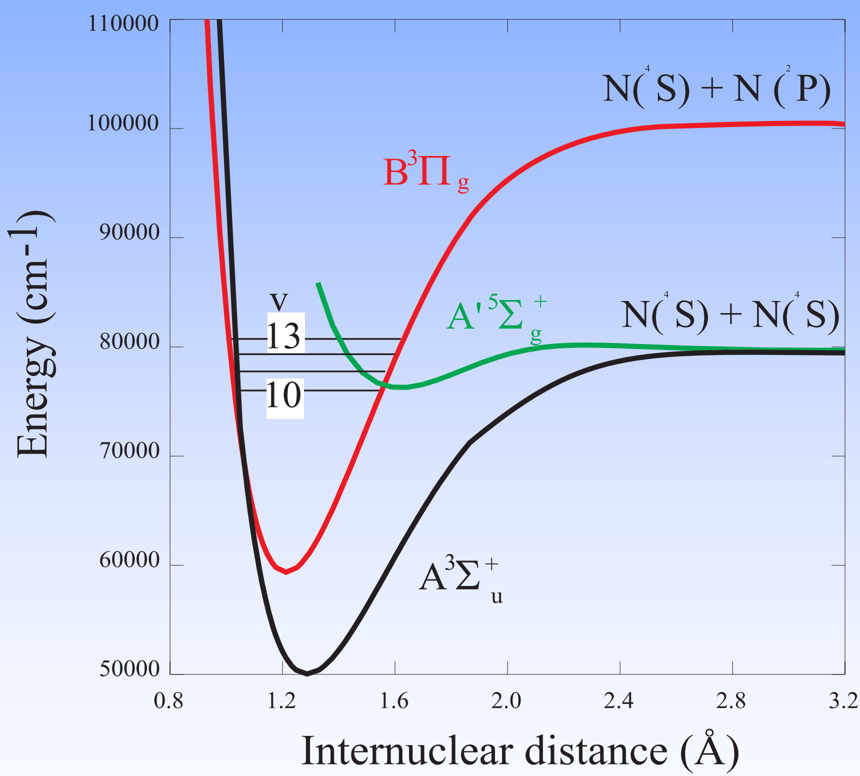

Overpopulation Factors $\rho_v$




- Excess of nitrogen atoms causes peak at v=13:

$N + N \rightarrow N_2$ (B, v=13) (Inverse Predissociation)

# Predissociation / Inverse Predissociation



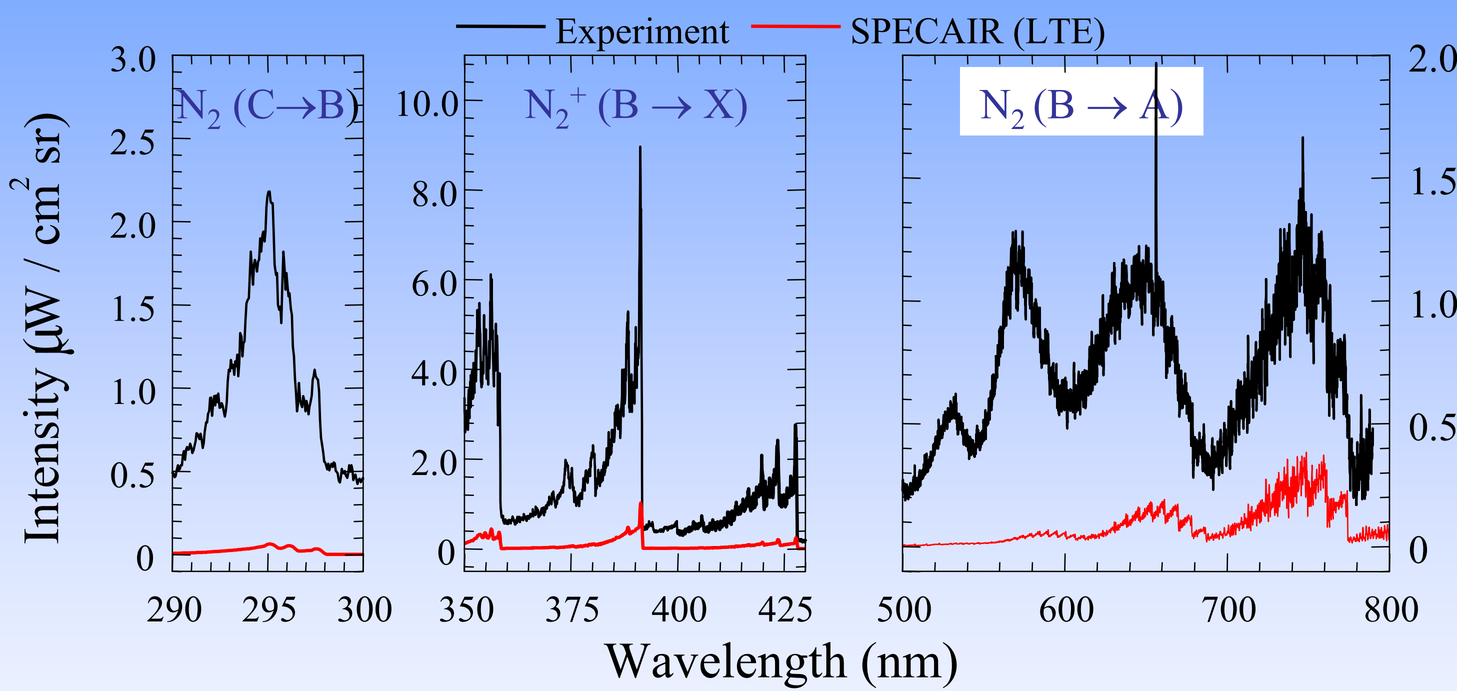

– Predissociation:

$N_2$ (B,v=13) ⇒ N + N

– Inverse Predissociation

N + N ⇒ $N_2$ (B,v=13)

# Emission spectrum at exit of test section




- $N_2^+$ B state overpopulated due to excess of electrons
- $N_2$ C state likely to be affected by predissociation (but rates are still unknown)

# Conclusions: long list of requests

- Term energies for high J's
- VUV/EUV experimental data:
  - $N_2$ transitions
  - NO transitions (in particular NO C-X, D-X, F-X)
- Infrared modeling data:
  - probabilities and lines for transitions between NO Rydberg states
  - $NO^+$ ground state term energies
- Predissociation linewidths:
  - $N_2$ C $^3\Pi$
  - NO C $^2\Pi$

www.specair-radiation.net