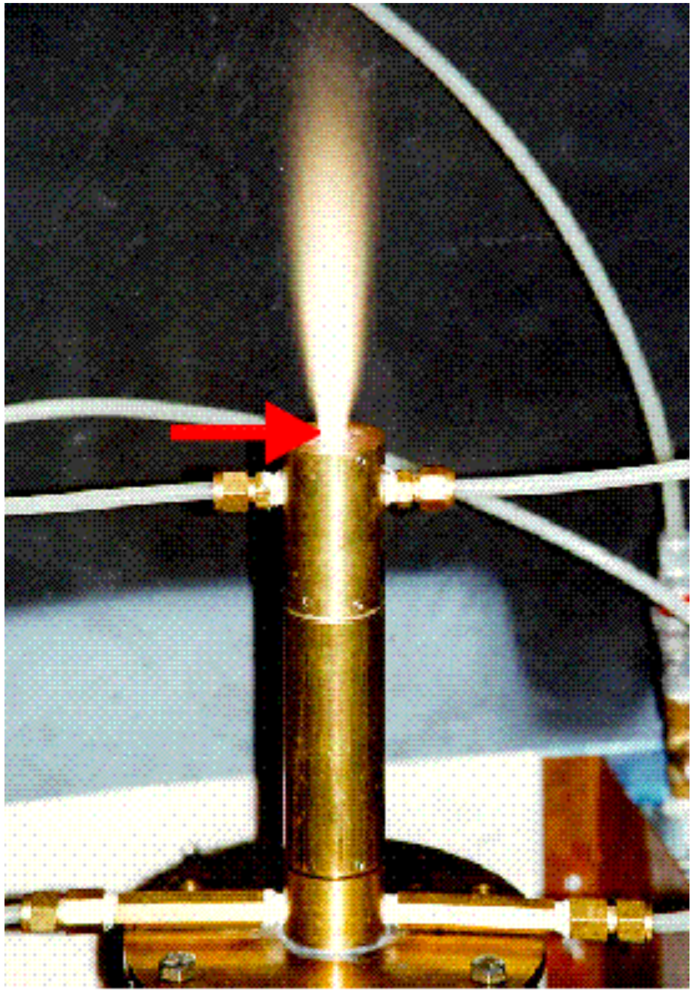
State-to-state modeling of a recombining nitrogen plasma experiment

Christophe O. Laux,
Richard J. Gessman, Laurent Pierrot

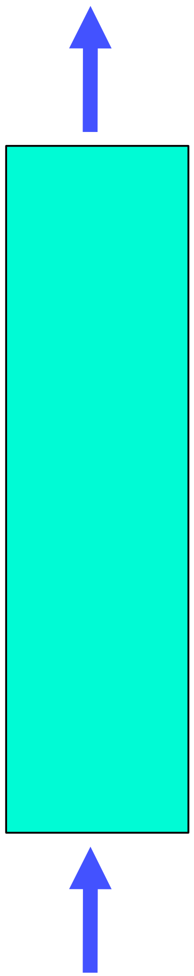
Ecole Centrale Paris, Laboratoire EM2C-CNRS
and
Stanford University, Mechanical Engineering Dept.

Symposium in Honour of Prof Mario Capitelli on the Occasion of His 70th Birthday
Università degli Studi di Bari - Aldo Moro
January 31- February 1, 2011

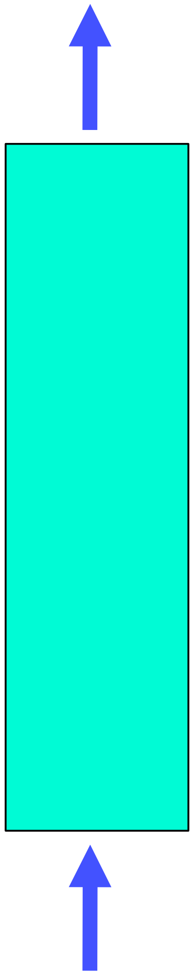
Recombining nitrogen plasma at atmospheric pressure



Recombining nitrogen plasma at atmospheric pressure



Recombining nitrogen plasma at atmospheric pressure



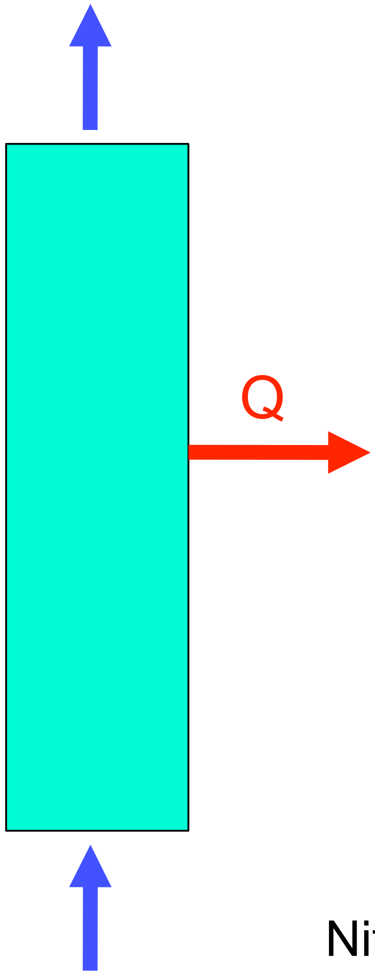
v ~ 1 km/s

TEST-SECTION INLET:

Nitrogen plasma in LTE at 7200 K

(N_2 highly dissociated)

Recombining nitrogen plasma at atmospheric pressure

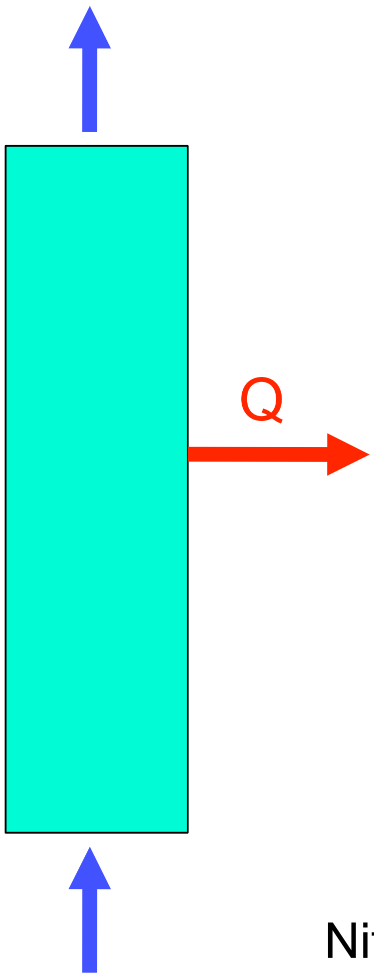


Fast cooling imposed
by water-cooled wall at 300 K

v ~ 1 km/s

TEST-SECTION INLET:
Nitrogen plasma in LTE at 7200 K
(N_2 highly dissociated)

Recombining nitrogen plasma at atmospheric pressure



Residence time: 250 μs

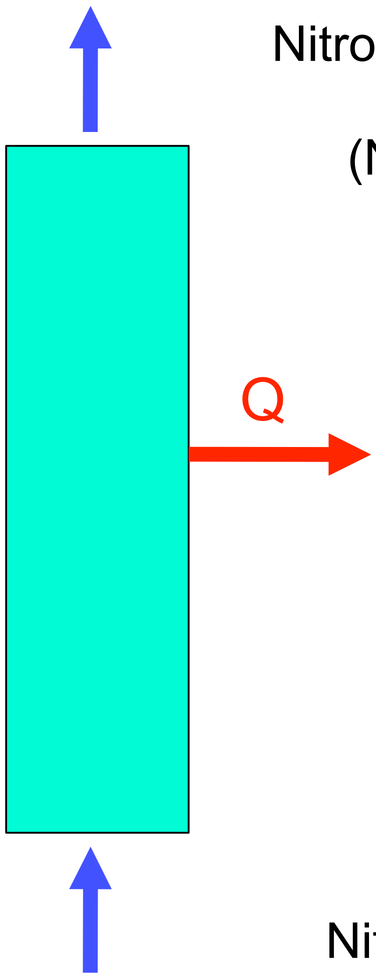
v ~ 1 km/s

Fast cooling imposed by water-cooled wall at 300 K

TEST-SECTION INLET:
Nitrogen plasma in LTE at 7200 K
(N_2 highly dissociated)

Recombining nitrogen plasma at atmospheric pressure

TEST-SECTION EXIT:
Nitrogen plasma in nonequilibrium
at T = 4850 K
(N population partly frozen)



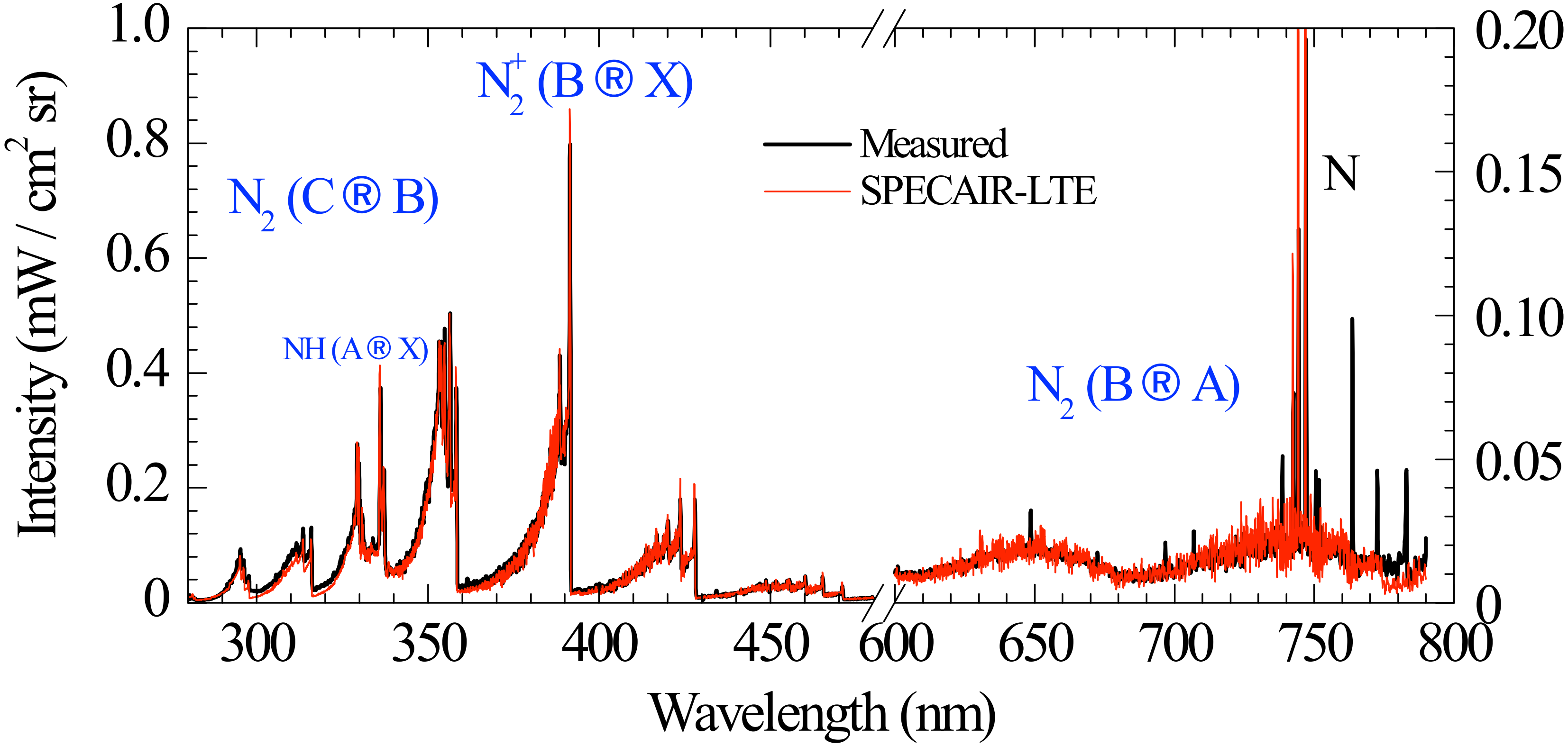
Residence time: 250 μs

Fast cooling imposed
by water-cooled wall at 300 K

v ~ 1 km/s

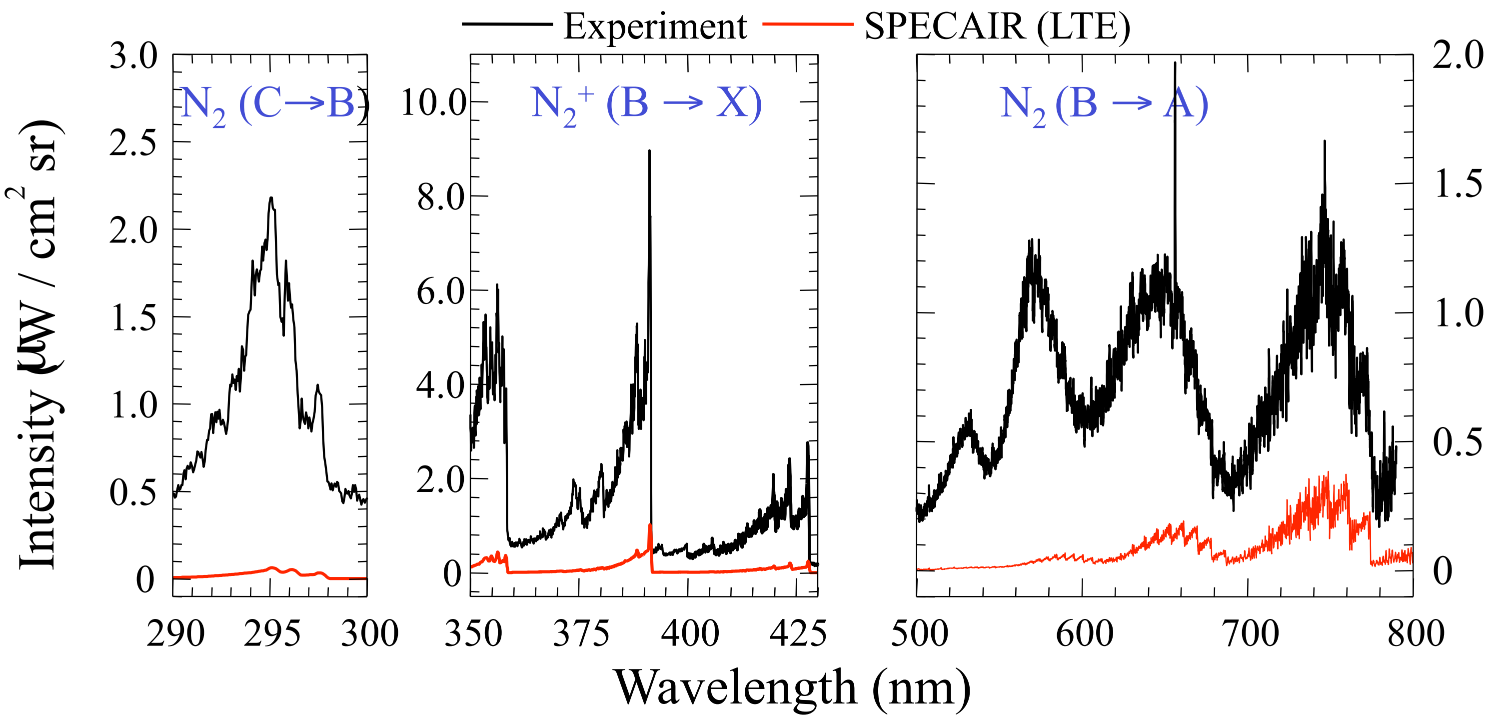
TEST-SECTION INLET:
Nitrogen plasma in LTE at 7200 K
(N_2 highly dissociated)

Emission Spectrum at Test-Section Inlet



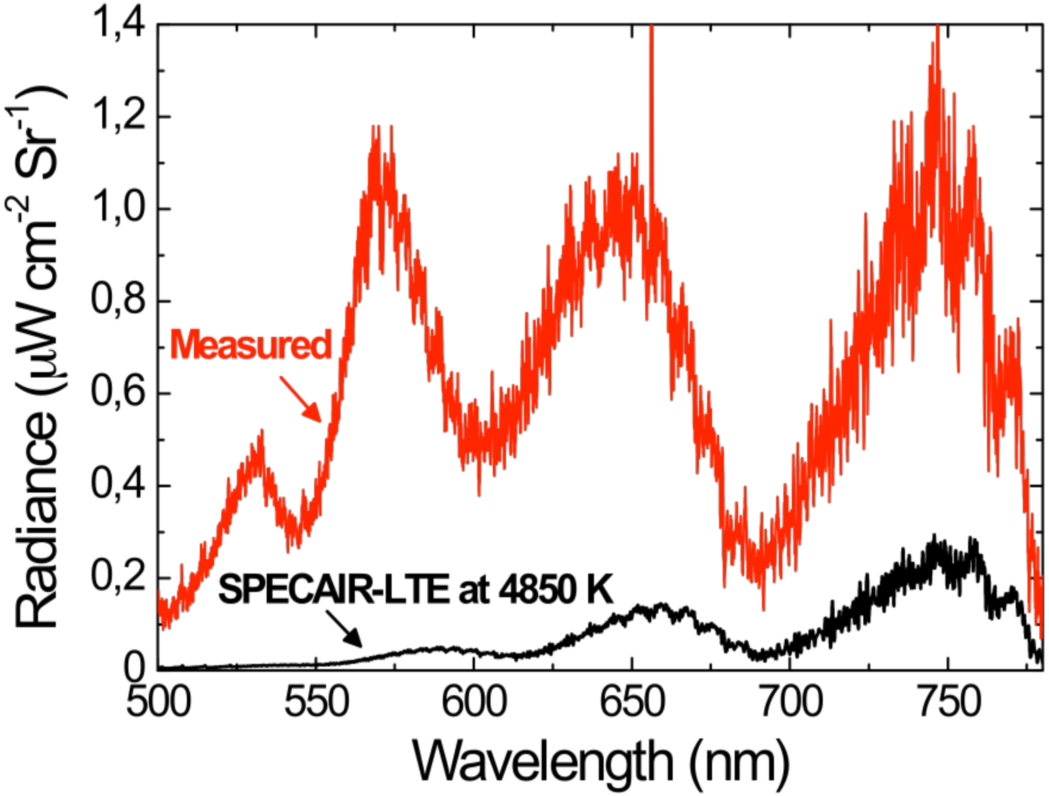
- Test-section inlet: Plasma close to LTE

Emission Spectrum at Test-Section Exit

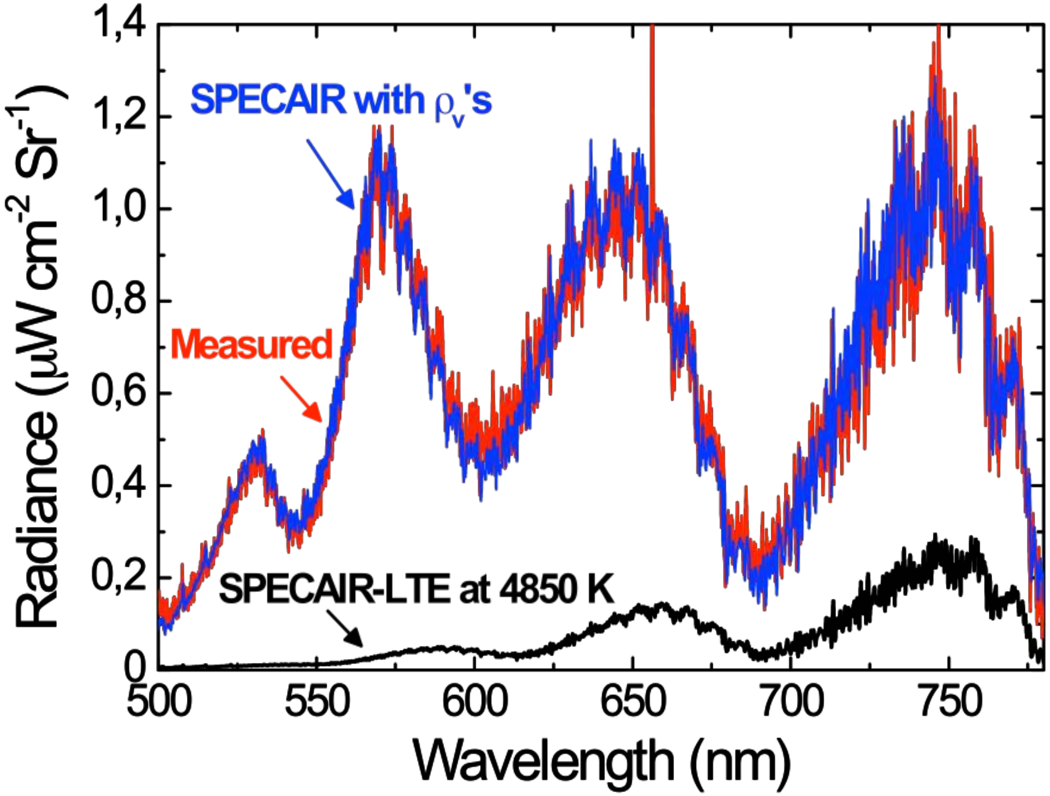


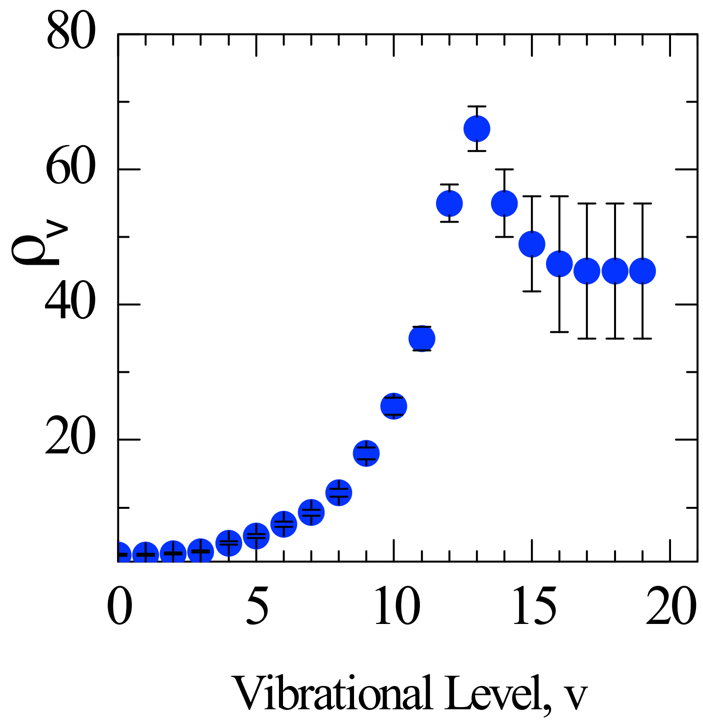
- Emitting states (N_2^+ B, N_2 C, N_2 B) are overpopulated with respect to LTE.

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

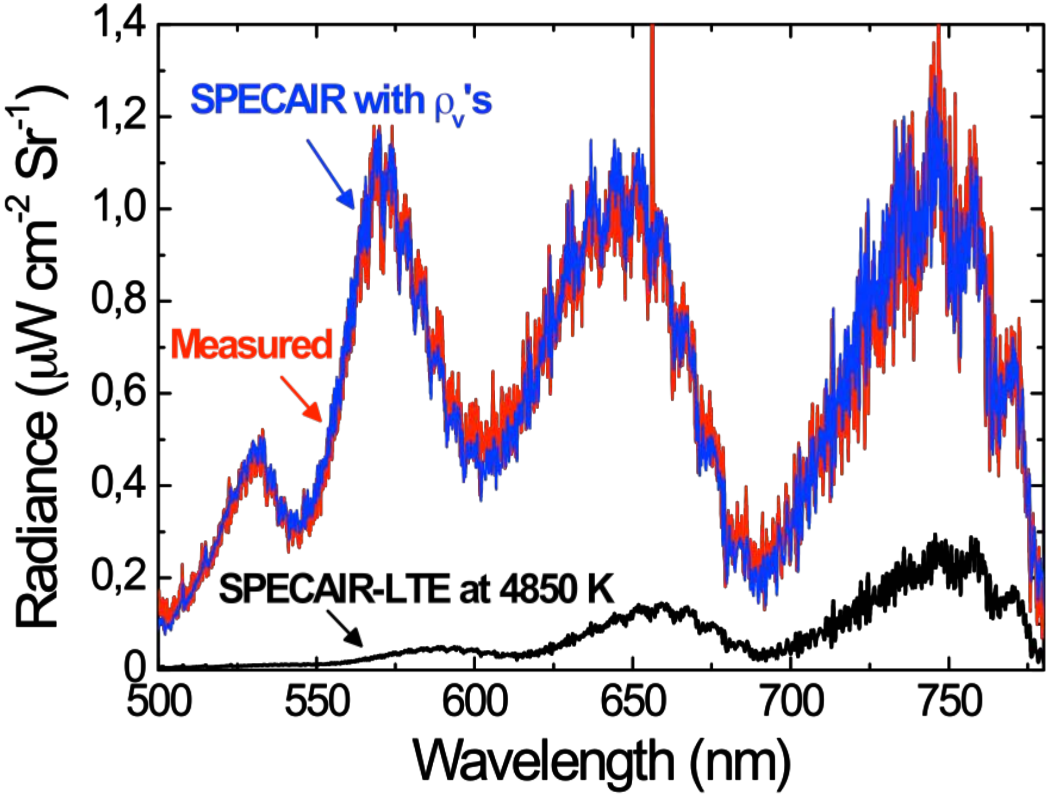


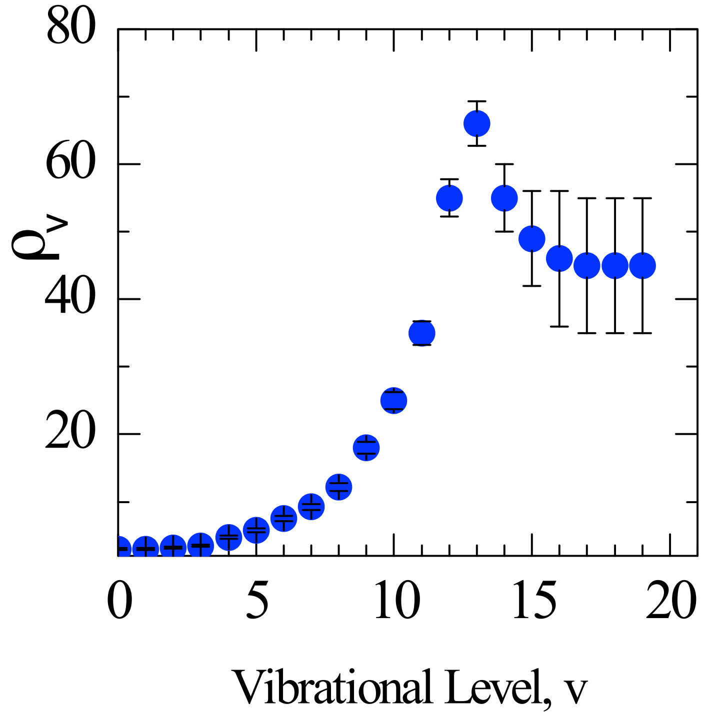
Analysis of the N_2 B-A spectrum at exit of test-section





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





- Non-Boltzmann distribution of the vibrational levels
  ⇒ CR model needed to analyze experiment

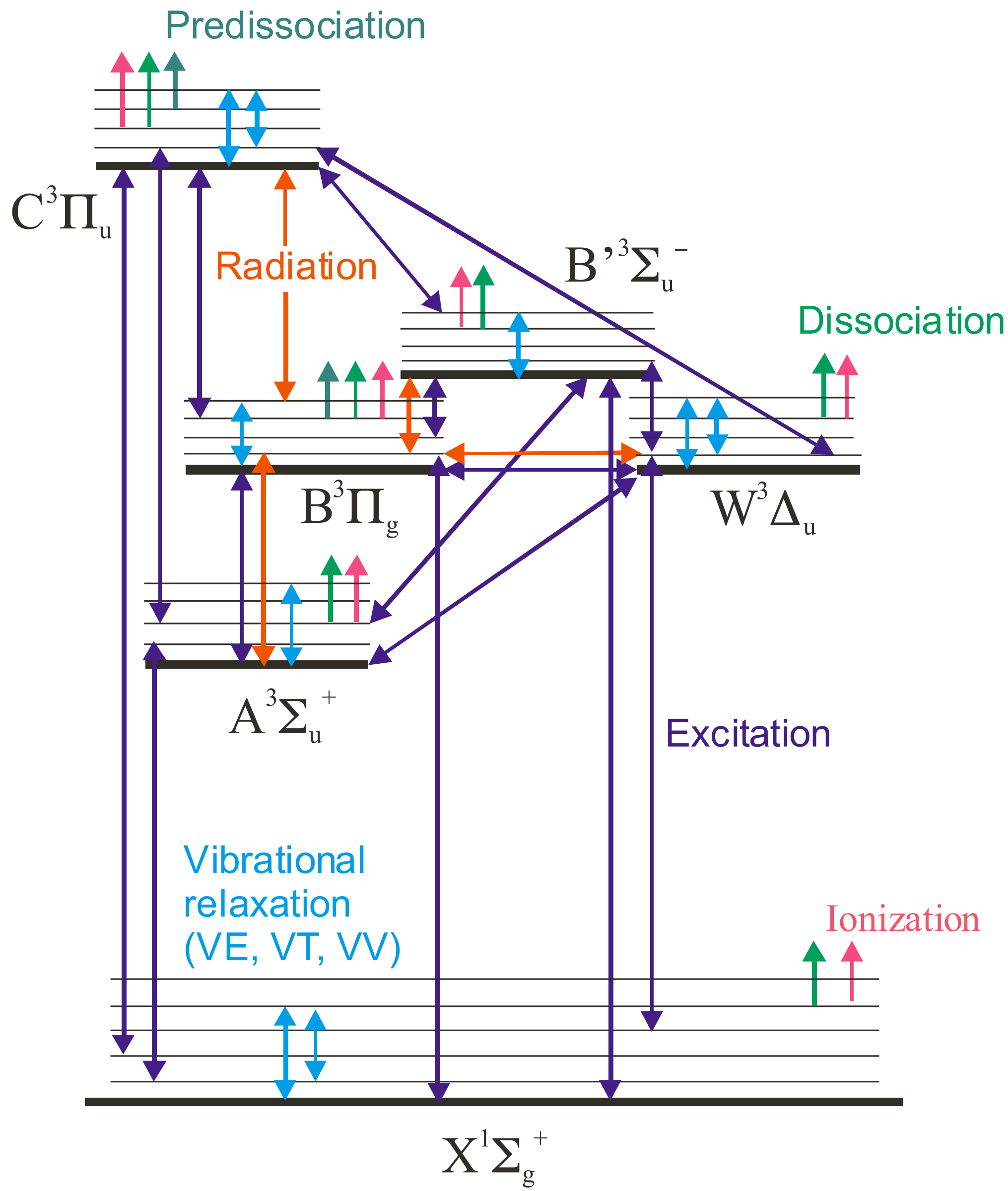
Vibrationally Specific State-to-State CR Model of nitrogen

- Predict nonequilibrium populations of
  - N (22 electronic levels)
  - N^+ (1 electronic level)
  - N_2 X (v=0-47), A (0-27), B (0-30), W(0-37), B' (0-41), C (0-4)
  - N_2^+ X (v=0-52), A (0-63), B (0-24)
  - Electrons

  $\Rightarrow$ 357 states + electrons

- Input parameters
  - Number density of N nuclei and electrons
  - P
  - T_e: kinetic temperature of electrons (Maxwellian)
  - T_g: kinetic temperature of heavy species (Maxwellian)
  - $T_{rot} = T_g$

Vibrationally Specific State-to-State CR Model of nitrogen



~46,000 state-to-state reactions

Collisional-Radiative Model of N_2

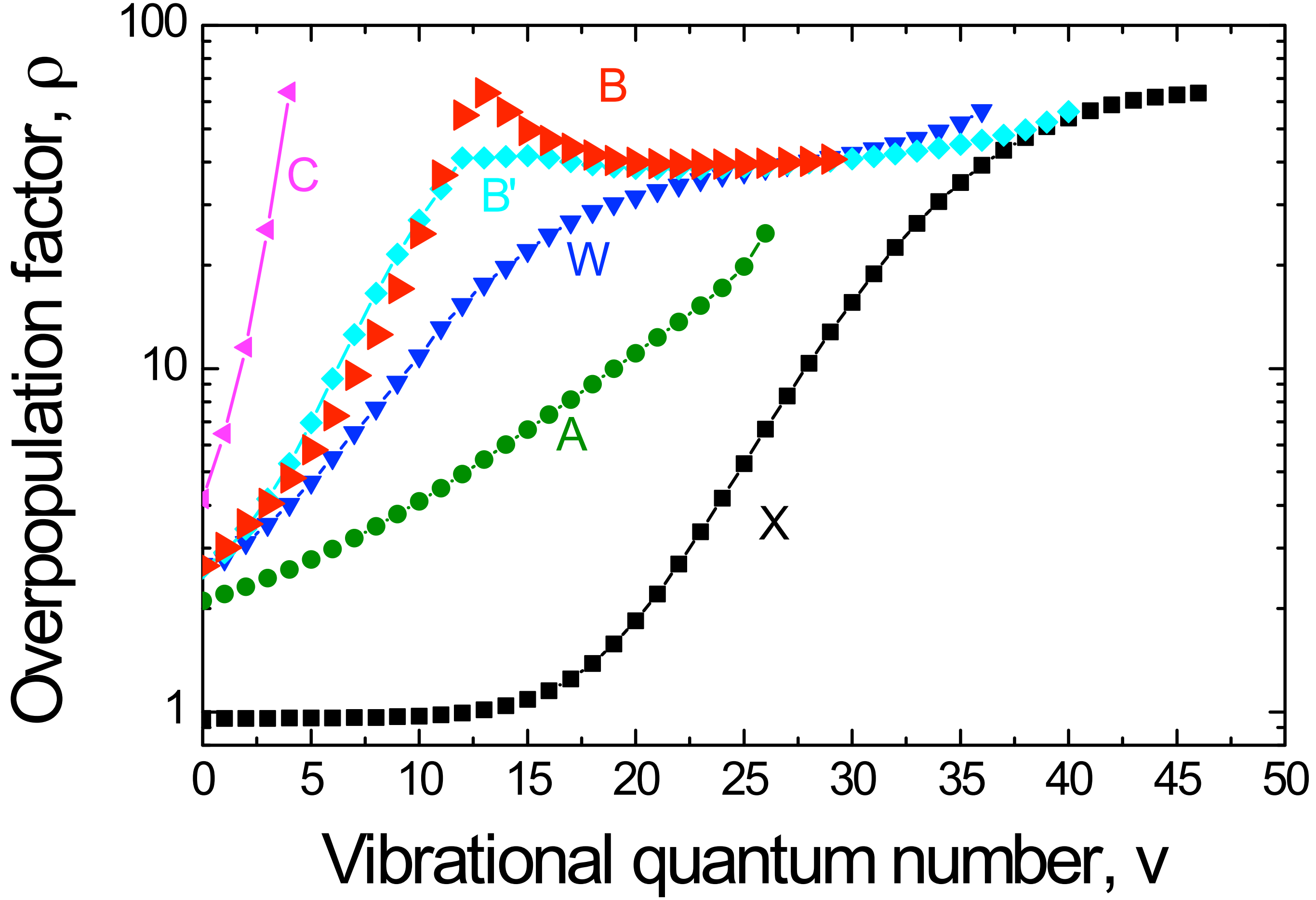
- Vibrational state-specific reactions considered:
  - Electron-impact excitation of N, N_2, N_2^+
  - Electron-impact ionization of N and N_2
  - Electron and heavy-particle impact dissociation of N_2 and N_2^+
  - Dissociative recombination of N_2^+
  - Charge exchange: $N_2^+ + N \Leftrightarrow N_2 + N^+$
  - VE: electron-impact vibrational excitation of N_2 X
  - VT: vibrational-translational transfer
  - VV: vibrational-vibrational transfer
  - Radiation
  - Predissociation

Assumptions for CR simulations at test-section exit

- P=1 atm and T=4850 K
- n_e=7.3×10^{13} cm^{-3} (measured value)
- n_N adjusted to provide best match to experiment
- EEDF is Maxwellian
  (Capitelli et al., JTHT, 12, 478-481, 1998)

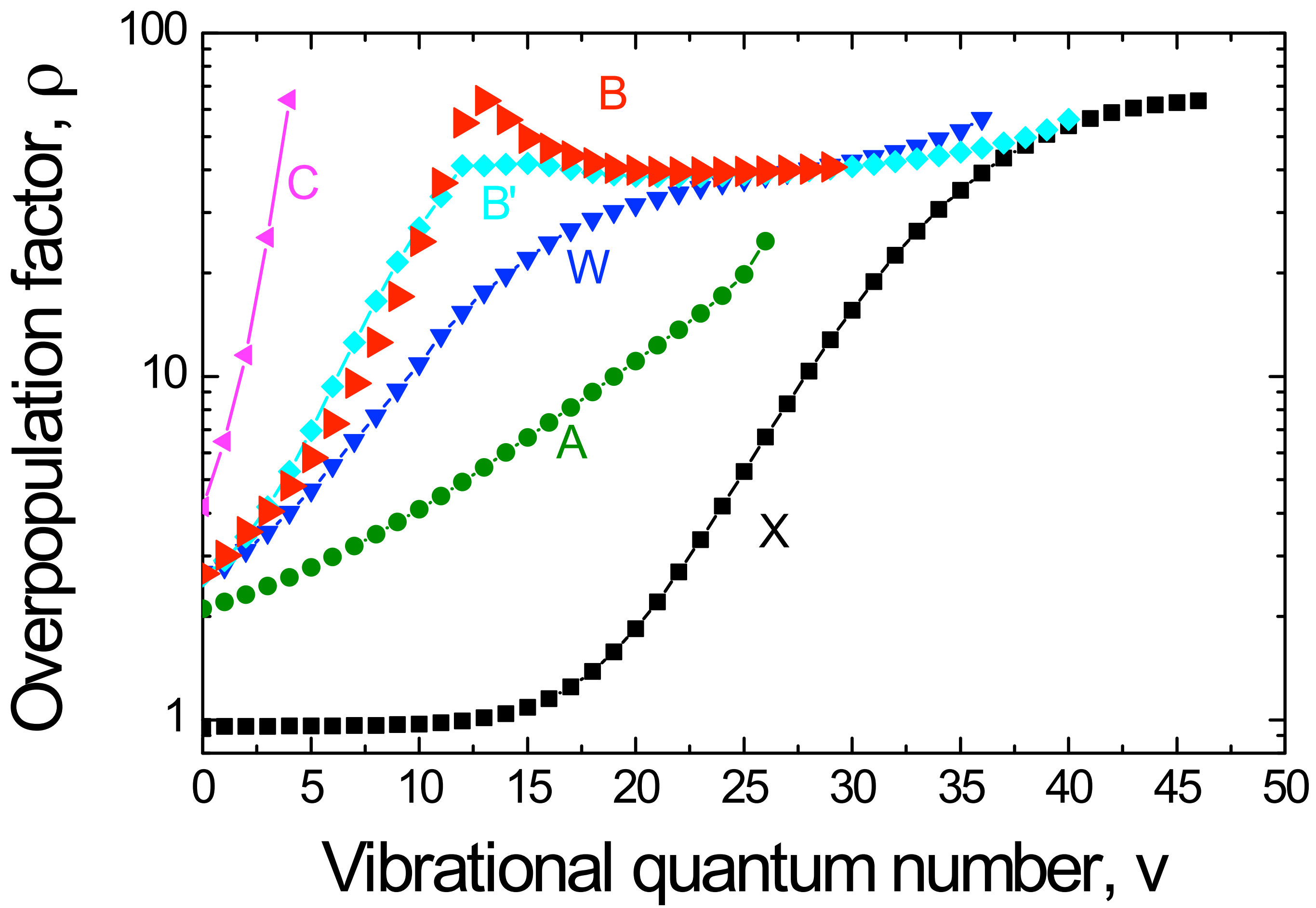
CR model results: vibronic distributions

T = 4850 K, P = 1 atm, ρ_e = 180, ρ_N = 8.1



CR model results: vibronic distributions

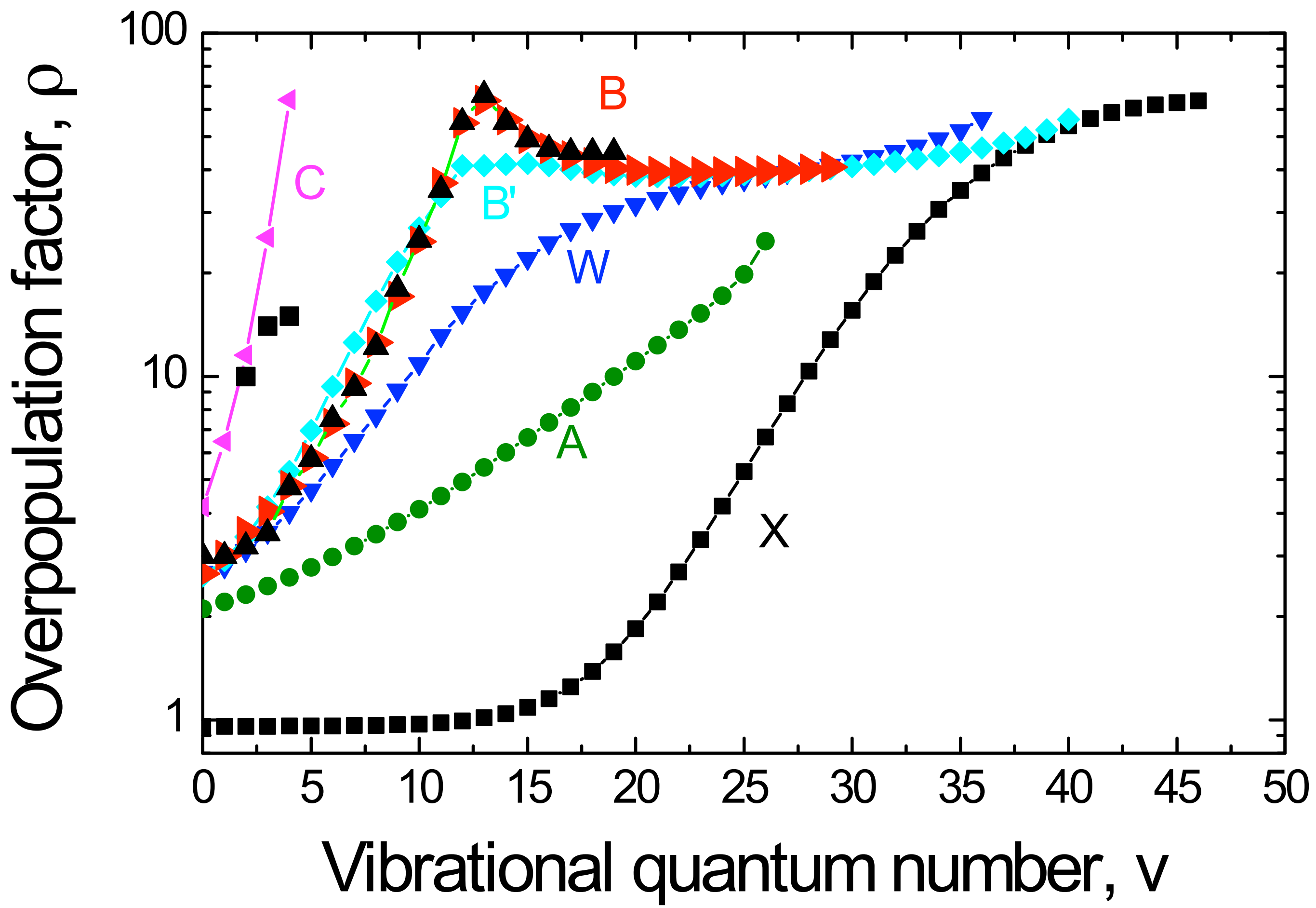
T = 4850 K, P = 1 atm, ρ_e = 180, ρ_N = 8.1



- Peak at v=13 is due to inverse predissociation: N + N → N_2 (B, v=13)

CR model results: comparison with experiment

T = 4850 K, P = 1 atm, ρ_e = 180, ρ_N = 8.1



- Peak at v=13 is due to inverse predissociation: N + N → N_2 (B, v=13)

Conclusions

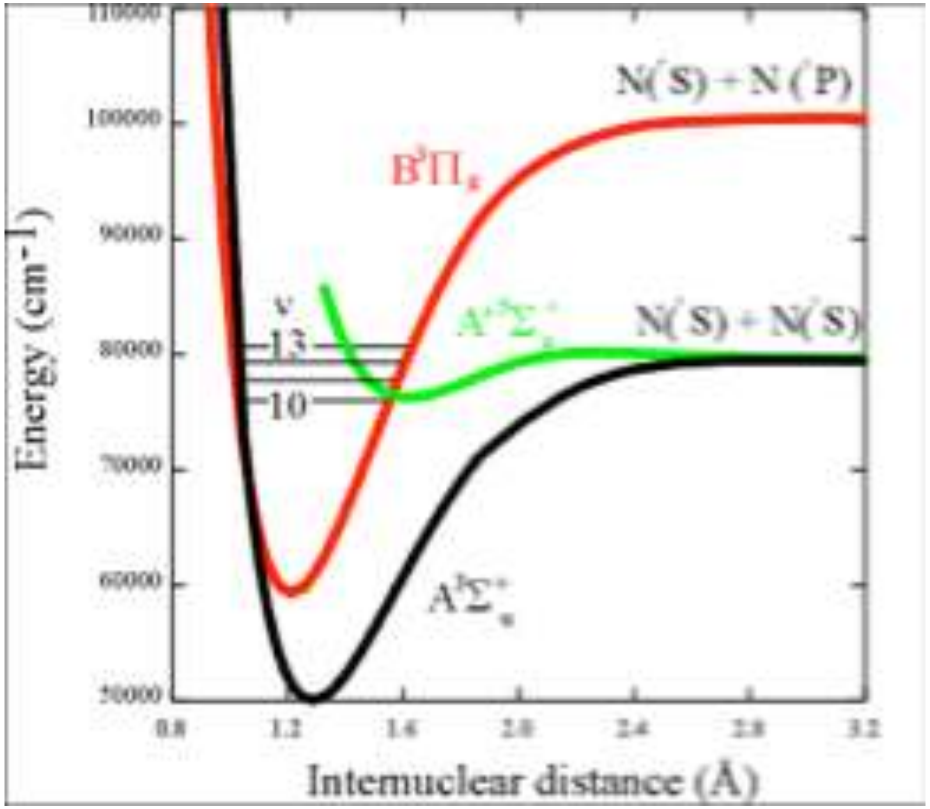
- State-to-state model developed to predict vibrational populations in ground and excited states of nitrogen
- Good agreement with measured vibrational distributions
- Overpopulation of N_2 B, v=13 provides a convenient way to measure absolute densities of N atoms by emission spectroscopy (application to expanding flows,…)

Conclusions

- State-to-state model developed to predict vibrational populations in ground and excited states of nitrogen
- Good agreement with measured vibrational distributions
- Overpopulation of N_2 B, v=13 provides a convenient way to measure absolute densities of N atoms by emission spectroscopy (application to expanding flows,…)

JOYEUX

Predissociation/Inverse Predissociation



- Predissociation:

  N_2 (B,v=13) $\Rightarrow$ N($^4S^o$) + N ($^4S^o$)

- Inverse Predissociation

  N($^4S^o$) + N ($^4S^o$) $\Rightarrow$ N_2 (B,v=13)

Rate equation for N_2, B, v=13

$$\frac{dn_{N_2,B,13}}{dt} = -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k_{VT}^{13\to 14} + k_{VT}^{13\to 12}\right) + n_e k^e_{ion} + \sum_{Y=X,A,B',W,C} n_e k^e_{B,13\to Y}\right\}$$
$$+ n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k_{VT}^{14\to 13} + n_{N_2,B,12} n_M k_{VT}^{12\to 13} + n_e^2 n_{N_2^+} k^e_{rec}$$
$$+ \sum_{Y=X,A,B',W,C} n_Y n_e k^e_{Y\to B,13}$$
$$= 0 \quad \text{at} \quad \text{steady-state}$$

Rate equation for N_2, B, v=13

$2.6\text{x}10^8\ s^{-1}$

$$\frac{dn_{N_2,B,13}}{dt} = -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k^{13\rightarrow 14}_{VT} + k^{13\rightarrow 12}_{VT}\right) + n_e k^e_{ion} + \sum_{Y=X,A,B',W,C} n_e k^e_{B,13\rightarrow Y}\right\}$$

$$+n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k^{14\rightarrow 13}_{VT} + n_{N_2,B,12} n_M k^{12\rightarrow 13}_{VT} + n_e^2 n_{N_2^+} k^e_{rec}$$

$$+\sum_{Y=X,A,B',W,C} n_Y n_e k^e_{Y\rightarrow B,13}$$

$$= 0 \quad \text{at} \quad \text{steady-state}$$

Rate equation for N_2, B, v=13

$2.6\times10^{8}\ s^{-1}$

$2\times10^{6}\ s^{-1}$

$$\frac{dn_{N_2,B,13}}{dt} = -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k^{13\rightarrow 14}_{VT} + k^{13\rightarrow 12}_{VT}\right) + n_e k^{e}_{ion} + \sum_{Y=X,A,B',W,C} n_e k^{e}_{B,13\rightarrow Y}\right\}$$

$$+ n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k^{14\rightarrow 13}_{VT} + n_{N_2,B,12} n_M k^{12\rightarrow 13}_{VT} + n_e^2 n_{N_2^+} k^{e}_{rec}$$

$$+ \sum_{Y=X,A,B',W,C} n_Y n_e k^{e}_{Y\rightarrow B,13}$$

$$= 0 \quad \text{at} \quad \text{steady-state}$$

Rate equation for N_2, B, v=13

$2.6\times10^{8}\ s^{-1}$

$2\times10^{6}\ s^{-1}$ $6\times10^{6}\ s^{-1}$

$$\frac{dn_{N_2,B,13}}{dt} = -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k_{VT}^{13\rightarrow 14} + k_{VT}^{13\rightarrow 12}\right) + n_e k^e_{ion} + \sum_{Y=X,A,B',W,C} n_e k^e_{B,13\rightarrow Y}\right\}$$

$$+ n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k_{VT}^{14\rightarrow 13} + n_{N_2,B,12} n_M k_{VT}^{12\rightarrow 13} + n_e^2 n_{N_2^+} k^e_{rec}$$

$$+ \sum_{Y=X,A,B',W,C} n_Y n_e k^e_{Y\rightarrow B,13}$$

$$= 0 \quad \text{at} \quad \text{steady-state}$$

Rate equation for N_2, B, v=13

2.6x10^{8} s^{-1} — 2x10^{6} s^{-1} — 6x10^{6} s^{-1} — ~0 s^{-1}

$$\frac{dn_{N_2,B,13}}{dt} = -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k^{13\rightarrow 14}_{VT} + k^{13\rightarrow 12}_{VT}\right) + n_e k^e_{ion} + \sum_{Y=X,A,B',W,C} n_e k^e_{B,13\rightarrow Y}\right\}$$

$$+ n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k^{14\rightarrow 13}_{VT} + n_{N_2,B,12} n_M k^{12\rightarrow 13}_{VT} + n_e^2 n_{N_2^+} k^e_{rec}$$

$$+ \sum_{Y=X,A,B',W,C} n_Y n_e k^e_{Y\rightarrow B,13}$$

$$= 0 \quad \text{at} \quad \text{steady-state}$$

Rate equation for N_2, B, v=13

$2.6\text{x}10^{8}\ s^{-1}$

$2\text{x}10^{6}\ s^{-1}$ $6\text{x}10^{6}\ s^{-1}$ $\sim 0\ s^{-1}$ $4.2\text{x}10^{6}\ s^{-1}$

$$
\begin{aligned}
\frac{dn_{N_2,B,13}}{dt} = & -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k_{VT}^{13 \circledR 14} + k_{VT}^{13 \circledR 12}\right) + n_e k^{e}_{ion} + \sum_{Y=X,A,B',W,C} n_e k^{e}_{B,13 \circledR Y}\right\} \\
& + n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k_{VT}^{14 \circledR 13} + n_{N_2,B,12} n_M k_{VT}^{12 \circledR 13} + n_e^2 n_{N_2^+} k^{e}_{rec} \\
& + \sum_{Y=X,A,B',W,C} n_Y n_e k^{e}_{Y \circledR B,13} \\
& = 0 \quad \text{at} \quad \text{steady-state}
\end{aligned}
$$

Rate equation for N_2, B, v=13

$2.6\times10^{8}\ s^{-1}$ $\quad 2\times10^{6}\ s^{-1}$ $\quad 6\times10^{6}\ s^{-1}$ $\quad \sim0\ s^{-1}$ $\quad 4.2\times10^{6}\ s^{-1}$

$$\frac{dn_{N_2,B,13}}{dt} = -n_{N_2,B,13}\left\{k^{pred}_{v=13} + \sum_{v''} A_{13v''} + n_M\left(k_{VT}^{13\rightarrow 14} + k_{VT}^{13\rightarrow 12}\right) + n_e k^{e}_{ion} + \sum_{Y=X,A,B',W,C} n_e k^{e}_{B,13\rightarrow Y}\right\}$$

$$+ n_N^2 k^{inv.pr.}_{v=13} + \sum_{Y',v'} n_{N_2,Y',v'} A_{v'13} + n_{N_2,B,14} n_M k_{VT}^{14\rightarrow 13} + n_{N_2,B,12} n_M k_{VT}^{12\rightarrow 13} + n_e^2 n_{N_2^+} k^{e}_{rec}$$

$$+ \sum_{Y=X,A,B',W,C} n_Y n_e k^{e}_{Y\rightarrow B,13}$$

$$= 0 \quad \text{at} \quad \text{steady-state}$$

$$n_{N_2,B,13} k^{pred}_{v=13} \approx n_N^2 k^{inv.pr.}_{v=13}$$

N_2 (B,v=13) ⇔ N + N

N atom concentration

Previous analysis: $k_{pred} n_{N_2(B,13)} \cong k_{inv.pred.} \left(n_N\right)^2$

Always true: $k_{pred} n^{equil}_{N_2(B,13)} = k_{inv.pred.} \left(n^{equil}_N\right)^2$

Thus: $$\frac{n_{N_2(B,13)}}{n^{equil}_{N_2(B,13)}} = \left(\frac{n_N}{n^{equil}_N}\right)^2 \Rightarrow \rho_N = \sqrt{\rho_{N_2(B,13)}}$$

N atom concentration

Previous analysis: $k_{pred} n_{N_2(B,13)} \cong k_{inv.pred.} \left(n_N\right)^2$

Always true: $k_{pred} n^{equil}_{N_2(B,13)} = k_{inv.pred.} \left(n^{equil}_N\right)^2$

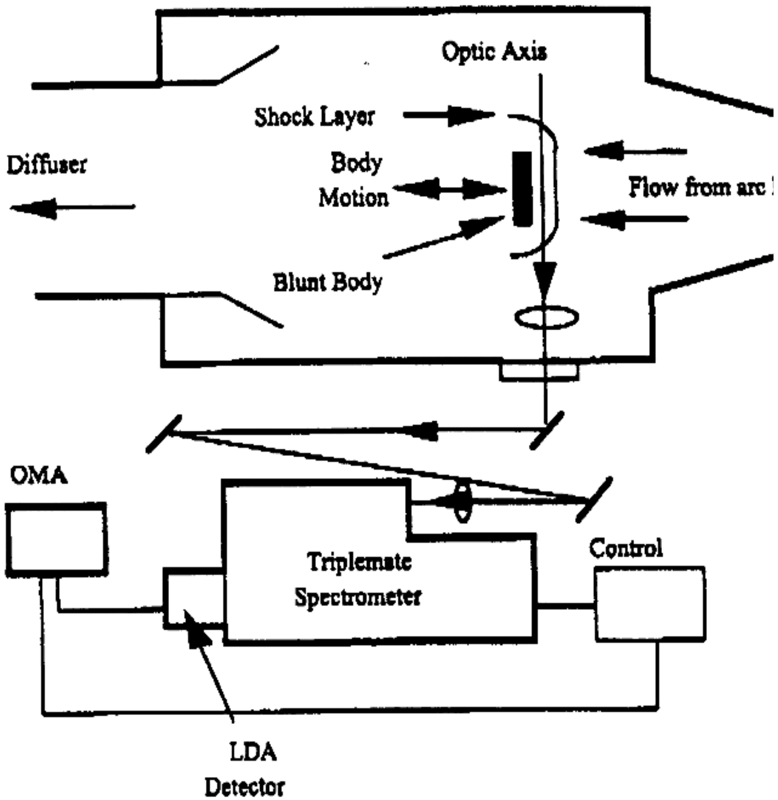
Thus: $\frac{n_{N_2(B,13)}}{n^{equil}_{N_2(B,13)}} = \left(\frac{n_N}{n^{equil}_N}\right)^2 \Rightarrow \rho_N = \sqrt{\rho_{N_2(B,13)}}$

- Diagnostic tool for ground state N concentration:
  - $\rho_{B,v=13} = 66 \pm 4$ (measured) $\Rightarrow \rho_N = 8.1 \pm 0.3$
  - $[N]^{eq,4850K} = 1.8 \times 10^{16}\ cm^{-3}$

$\Rightarrow [N] = 1.5 \pm 0.4 \times 10^{17}\ cm^{-3}$

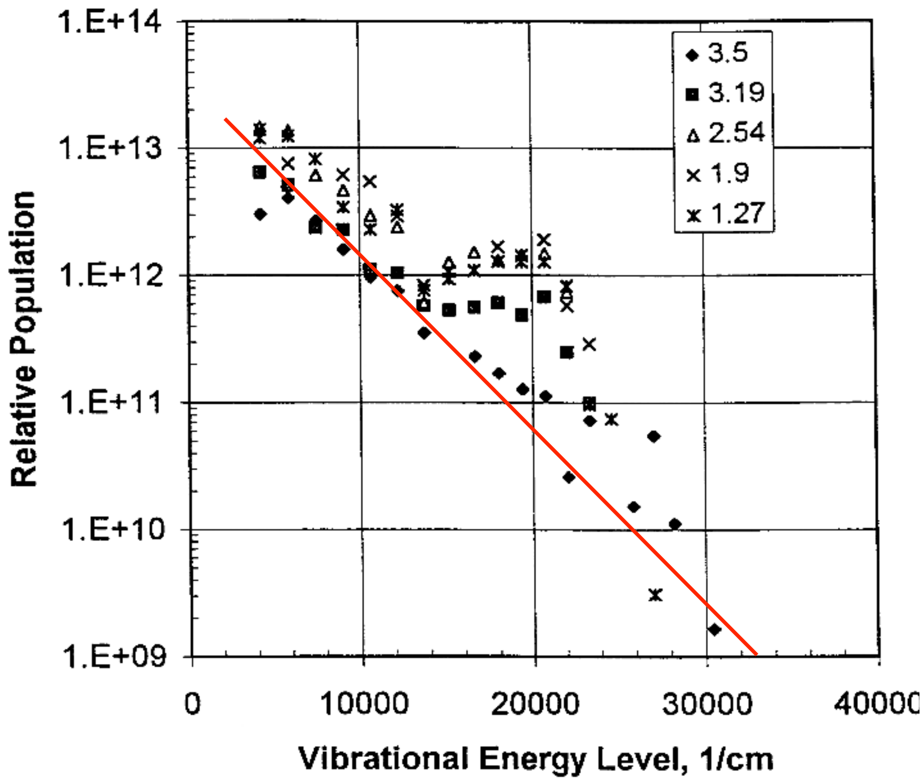
Nonequilibrium distribution of N2 B state in arcjet measurements at Johnston Space Center

Experimental set-up

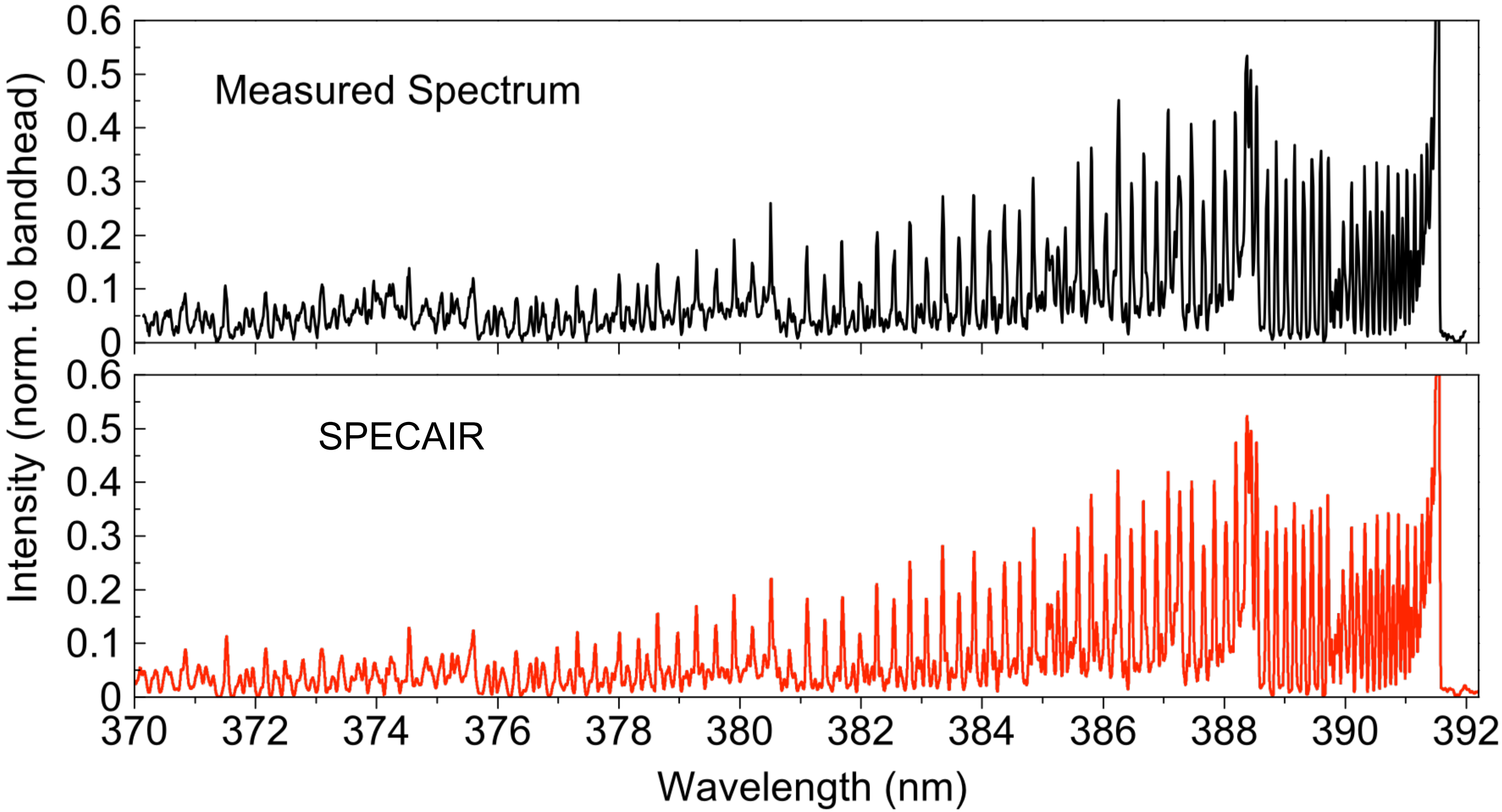


Blackwell, Scott, and Arepalli, JSC, 1997

N_2 B state vibrational populations as a function of distance from body

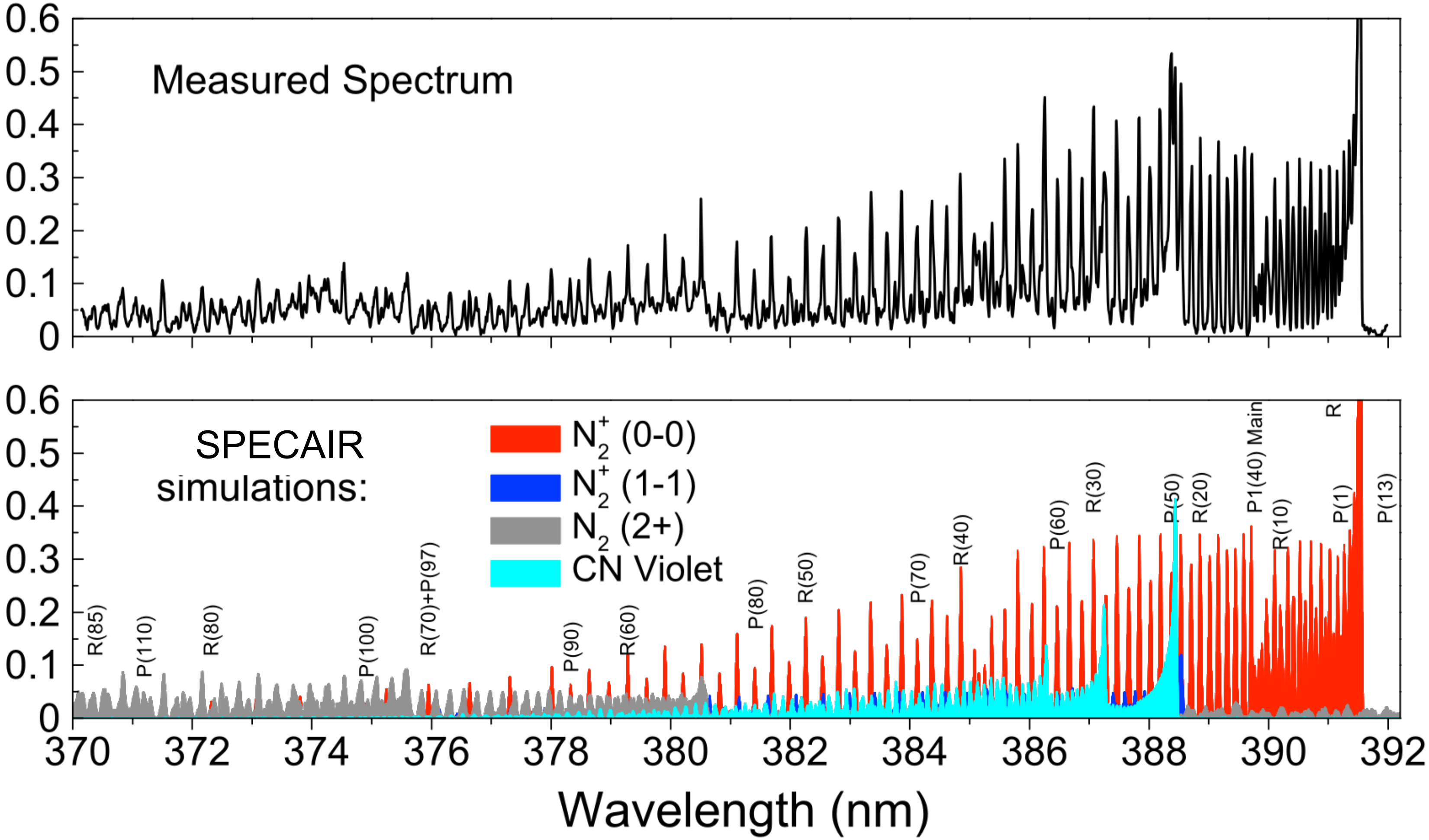


Rotational temperature at 15 cm using N_2^+

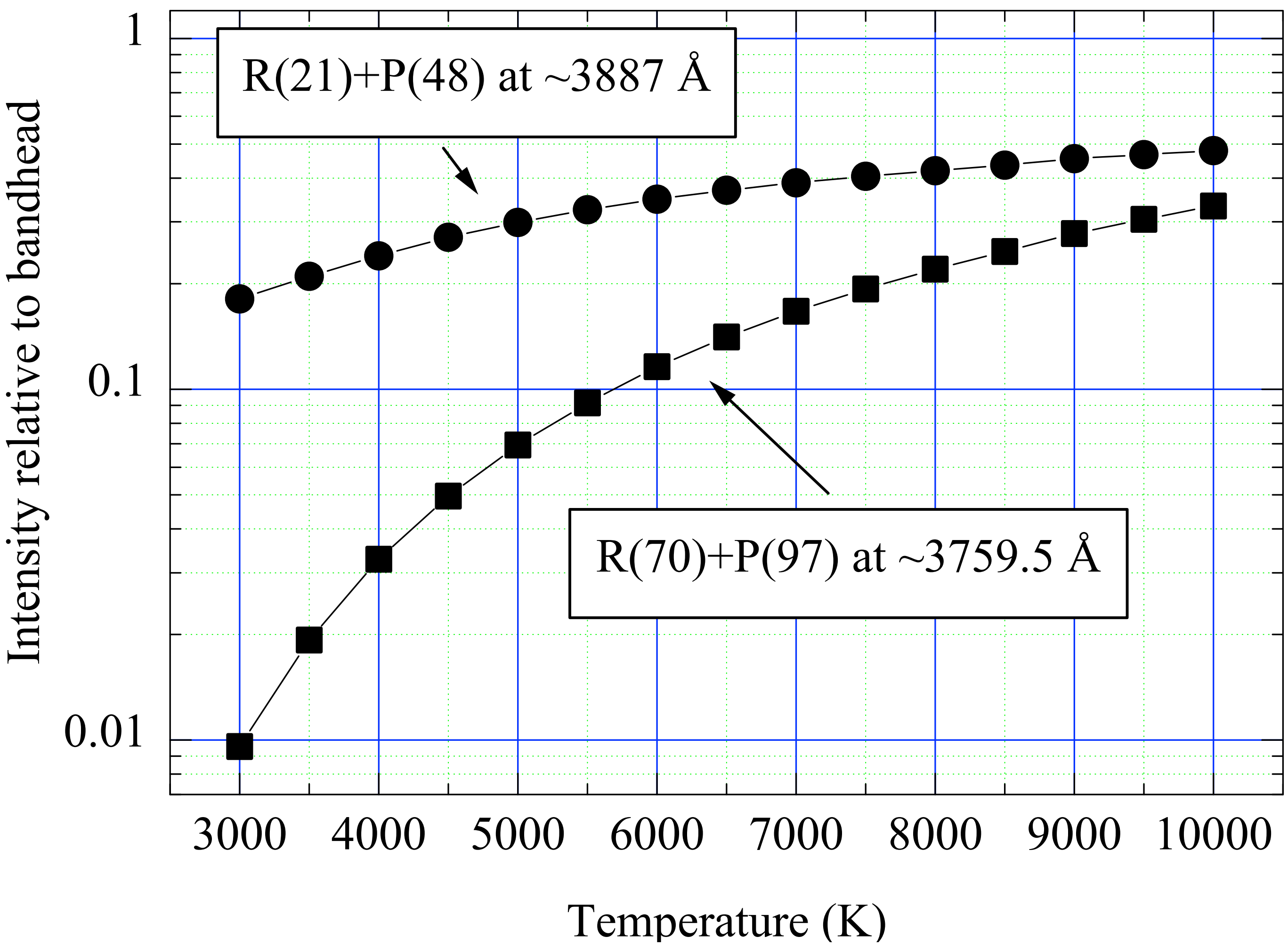


- Best fit: $T_{rot} = T_{vib} = 4850 \pm 100$ K

Rotational Temperature at 15 cm using N_2^+



Rotational temperature: [R(70)+P(97)] vs. Bandhead



Calculation of vibrational state specific rate coeff.

Example: N_2 (X, v") + e → N_2^+ (A, v') + e + e

- Rovibrational state-specific rate coefficient:

$$K_{N_2Xv''J''}^{N_2^+Av'J'}(T_e) = \frac{8\pi}{\sqrt{m_e}} \frac{1}{(2\pi k T_e)^{3/2}} \int_0^{+\infty} \varepsilon \sigma_{N_2Xv''J''}^{N_2^+Av'J'}(\varepsilon) \exp\left(-\frac{\varepsilon}{kT_e}\right) d\varepsilon$$

$$\sigma_{N_2Xv''J''}^{N_2^+Av'J'} = q_{Xv''}^{Av'}\, \delta_{J''}^{J'} \chi\left(\varepsilon, \Delta E_{Xv''J''}^{Av'J'}\right)$$

Calculation of vibrational state specific rate coeff.

Example: $N_2 (X, v'') + e \rightarrow N_2^+ (A, v') + e + e$

- Rovibrational state-specific rate coefficient:

$$K_{N_2Xv''J''}^{N_2^+Av'J'}(T_e) = \frac{8\pi}{\sqrt{m_e}} \frac{1}{(2\pi k T_e)^{3/2}} \int_0^{+\infty} \varepsilon \sigma_{N_2Xv''J''}^{N_2^+Av'J'}(\varepsilon) \exp\left(-\frac{\varepsilon}{kT_e}\right) d\varepsilon$$

$$\sigma_{N_2Xv''J''}^{N_2^+Av'J'} = q_{Xv''}^{Av'} \, \delta_{J''}^{J'} \chi\left(\varepsilon, \Delta E_{Xv''J''}^{Av'J'}\right)$$

$$\chi\left(\varepsilon, \Delta E_{Xv'J'}^{Av'J'}\right) = 4\pi a_0^2 N \left(\frac{R}{\Delta E_{Xv''J''}^{Av'J'}}\right)^2 \frac{1}{t+u+1} \left[\frac{\ln t}{2}\left(1 - \frac{1}{t^2}\right) + 1 - \frac{1}{t} - \frac{\ln t}{t+1}\right]$$

$$t = \varepsilon / \Delta E_{Xv''J''}^{Av'J'}, \qquad u = U / \Delta E_{Xv''J''}^{Av'J'}$$

Calculation of vibrational state specific rate coeff.

Example: N_2 (X, v”) + e → N_2^+ (A, v’) + e + e

- Rovibrational state-specific rate coefficient:

$$K_{N_2Xv''J''}^{N_2^+Av'J'}(T_e)=\frac{8\pi}{\sqrt{m_e}}\frac{1}{(2\pi kT_e)^{3/2}}\int_0^{+\infty}\varepsilon\sigma_{N_2Xv''J''}^{N_2^+Av'J'}(\varepsilon)\exp\left(-\frac{\varepsilon}{kT_e}\right)d\varepsilon$$

$$\sigma_{N_2Xv''J''}^{N_2^+Av'J'}=q_{Xv''}^{Av'}\,\delta_{J''}^{J'}\chi\left(\varepsilon,\Delta E_{Xv''J''}^{Av'J'}\right)$$

$$\chi\left(\varepsilon,\Delta E_{Xv'J'}^{Av'J'}\right)=4\pi a_0^2N\left(\frac{R}{\Delta E_{Xv''J''}^{Av'J'}}\right)^2\frac{1}{t+u+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right]$$

$$t=\varepsilon/\Delta E_{Xv''J''}^{Av'J'},\qquad u=U/\Delta E_{Xv''J''}^{Av'J'}$$

- Average over rotational levels (in Boltzmann distribution at T_r):

$$K_{N_2Xv''}^{N_2^+Av'}(T_e,T_r)=\frac{1}{Q_{rot}^{N_2Xv''}(T_r)}\times\sum_{J''}(2J''+1)\exp\left[-\frac{F_{N_2Xv''}(J'')}{kT_r}\right]\sum_{J'}K_{N_2Xv''J''}^{N_2^+Av'J'}(T_e)$$