Temperature Dependence of the UV Fluorescence Yield in Nitrogen and in Dry Air

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Fluorescence Yield:

$$Y_{v'v''}(P,T) = A_{v'v''}\ \tau_{v'}^{eff}(P,T)\ N_{v'}^{exc}(P,T) \qquad \text{(ph/MeV)}$$

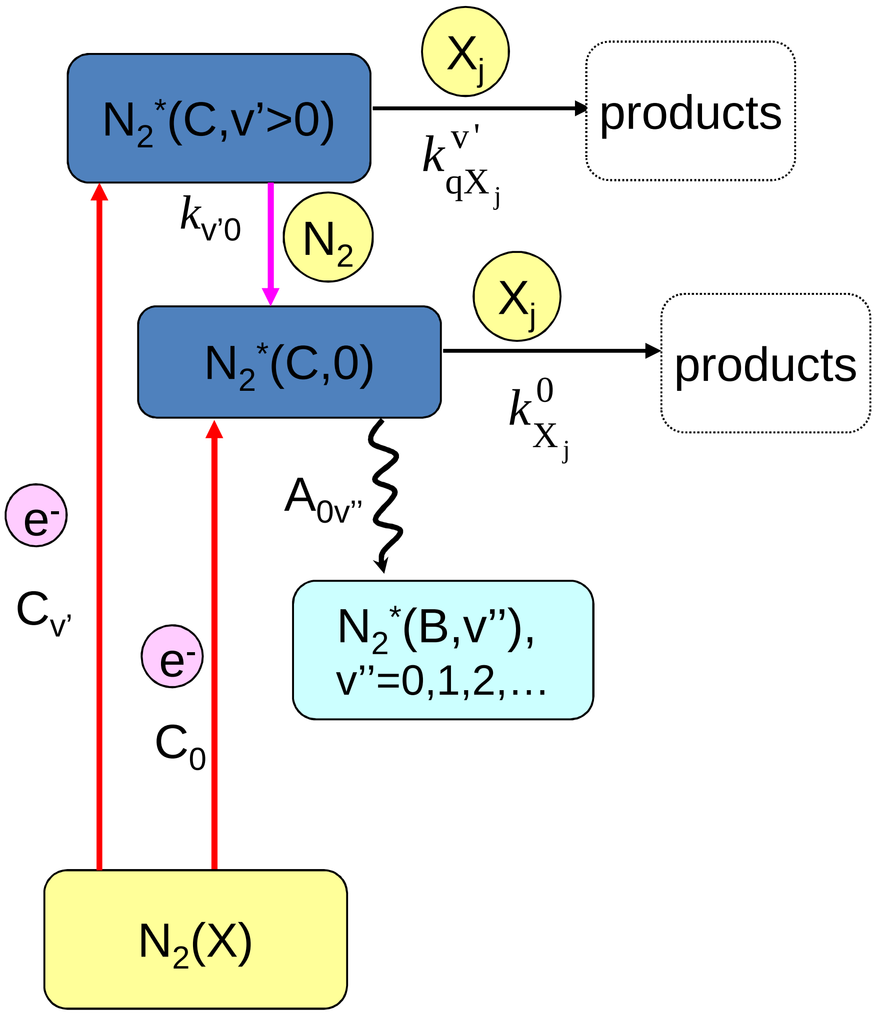
Two methods:

- Time resolved measurements $\Rightarrow\ R_{v'}(P,T) = 1/\tau_{v'}^{eff}(P,T)$
- Light intensity measurements $\Rightarrow\ I_{v'v''}(P,T) = P\ \eta(\lambda,T)\ Y_{v'v''}(P,T)$

$$I_{v'v''}^{corr} \propto \frac{N_{v'}^{exc}(P,T)}{R_{v'}(P,T)}$$

If only direct excitation is possible : $I_{v'v''}^{corr} \propto \dfrac{1}{R_{v'}(P,T)}$

Kinetic Model and Decay Rates



$X_j = N_2, O_2, H_2O, Ar, CO_2, \ldots$

$$R_{v'}(P,T) = \frac{1}{\tau_{v'}^{eff}} = A_{v'} + \sum_j k_{X_j}^{v'}(T)\, f_{X_j} N$$

$$A_{v'} = \sum_{v''} A_{v'v''} = \frac{1}{\tau_{v'}^{o}}$$

$$N = \frac{N_A}{R}\frac{p}{T} = 7.243\times 10^{18}\,\frac{p(hPa)}{T(K)}\ cm^{-3}$$

$$k_{v'}(T)\, N = \mathrm{k}_{v'}(T)\, p$$

$$\mathrm{k}_{v'}(T) = \frac{N_A}{R}\frac{1}{T} k_{v'}(T)$$

At room temperature (T_0),

$$R_{v'}(P) = A_{v'} + \sum_j k_{X_j}^{v'} f_{X_j} p_0 = A_{v'}\left(1 + \frac{p_0}{p'_{v'}}\right)$$

with $$\frac{1}{p'_{v'}} = \sum_j \frac{f_{X_j}}{p'_{v',X_j}};$$ and $$p'_{v',X_j} = \frac{A_{v'}}{k_{X_j}^{v'}}$$

$$\frac{1}{p'_{air,v'}} = \frac{f_{N2}}{p'_{N_2,v'}} + \frac{f_{O2}}{p'_{O_2,v'}}$$

When T changes and gas density is kept constant,

$$R_{v'}(T) = A_{v'} + \sum_j k_{X_j}^{v'}(T)\, f_{X_j} N = A_{v'}\left(1 + \frac{p}{p'_{v'}(T)}\right)$$

$$p = p_0 \frac{T}{T_0}$$

Temperature dependence of the quenching rate constant

$$k_{v'}(T) = \langle v \rangle \sigma(T) = \sqrt{\frac{8k_B T}{\pi\mu}}\sigma(T)$$

Possible explanations for a negative temperature dependence of the collisional cross section *(see S. Rodrigues, 7th AFWS, Coimbra, Set. 2010)* :

- ✓ The process is very exothermic
- ✓ Absence of barriers for the process
- ✗ The process is governed by very long-range attractive forces $V(R) \sim \frac{C_n}{R^n},\ n < 4$
- ? Quenching proceeds through the formation of complexes

Dependence laws:

i) $\sigma(T) = c_1 \exp\left(\frac{c_2}{T}\right)$

ii) $\sigma(T) = c_1 \left(\frac{T}{T_0}\right)^{\alpha}$ (power law)

Power law ⇒

$$k_{v'}(T) = k_{v'}(T_0)\left(\frac{T}{T_0}\right)^{\alpha_{v'}+0.5} \quad (cm^3\ s^{-1})$$

$$k_{v'}(T) = k_{v'}(T_0)\left(\frac{T}{T_0}\right)^{\alpha_{v'}-0.5} \quad (hPa^{-1}\ s^{-1})$$

$$p'_{v'}(T) = p'_{v'}(T_0)\left(\frac{T_0}{T}\right)^{\alpha_{v'}-0.5} \quad (hPa)$$

$$k_{v'}(T) = \frac{N_A}{R}\frac{1}{T}k_{v'}(T)$$

$$\beta_{v'} = \alpha_{v'} + 0.5$$

- Time resolved measurements (@ constant gas density) yield

$$k_{v',N2}(T) = \frac{R_{v'}(T) - A_{v'}}{N} \quad (cm^3 s^{-1})$$

for pure N_2

$$k_{v',O2}(T) = \frac{R_{v'}(T) - A_{v'} - k_{v',N2}(T) N_{N2}}{N_{O2}} \quad (cm^3 s^{-1})$$

for N_2/O_2 mixtures

- @ constant gas density, light intensity for a given v'-v'' band varies with T according to (neglecting the vibrational relaxation mechanisms) :

$$\frac{1}{I^{corr}_{v'v''}(p_0,T)} \propto 1+\frac{p_0}{p'_{v'}(T_0)}\left(\frac{T}{T_0}\right)^{\beta_{v'}}$$

for pure N_2

Fraga et al., NIMA 597 (2008)

$$\frac{1}{S_{v'v''}} \propto 1+\frac{p}{p'^{air}_{v'}(T_0)}\left(\frac{T}{T_0}\right)^{\alpha^{air}_{\lambda}-0.5} = 1+\frac{p_0}{p'^{air}_{v'}(T_0)}\left(\frac{T}{T_0}\right)^{\beta^{air}_{\lambda}}$$

for N_2/O_2 (79:21)

M. Ave et al. NIM A597 (2008) 50

$$\beta^{air}_{\lambda} = \alpha^{air}_{\lambda} + 0.5$$

with

$$\frac{p_0}{p'^{air}_{v'}}\left(\frac{T}{T_0}\right)^{\beta^{air}_{\lambda}} = \left[\frac{f_{N_2}}{p'^{N_2}_{v'}(T_0)}\left(\frac{T}{T_0}\right)^{\beta^{N_2}_{v'}} + \frac{f_{O_2}}{p'^{O_2}_{v'}(T_0)}\left(\frac{T}{T_0}\right)^{\beta^{O_2}_{v'}}\right] p_0$$

Experimental results:

1) Light Yield measurements @ Coimbra (*Fraga et al., NIMA 597 (2008)*) :

- pure N_2 ;
- Excitation source : α-particles from Am-241
- Wavelength: (0,0) band centered at 337 nm selected with an IF (λ_c =340 nm, $\Delta\lambda$=10 nm);
- P = 300 – 700 hPa;
- T = -20^{o}C – 25^o C ;
- Experimental counting rates are corrected for geometric factors, variation of the transmission of the IF with angle of incidence and temperature, variation of the response of the PMT with T and takes into account the spectral distribution of light (as a function of T).

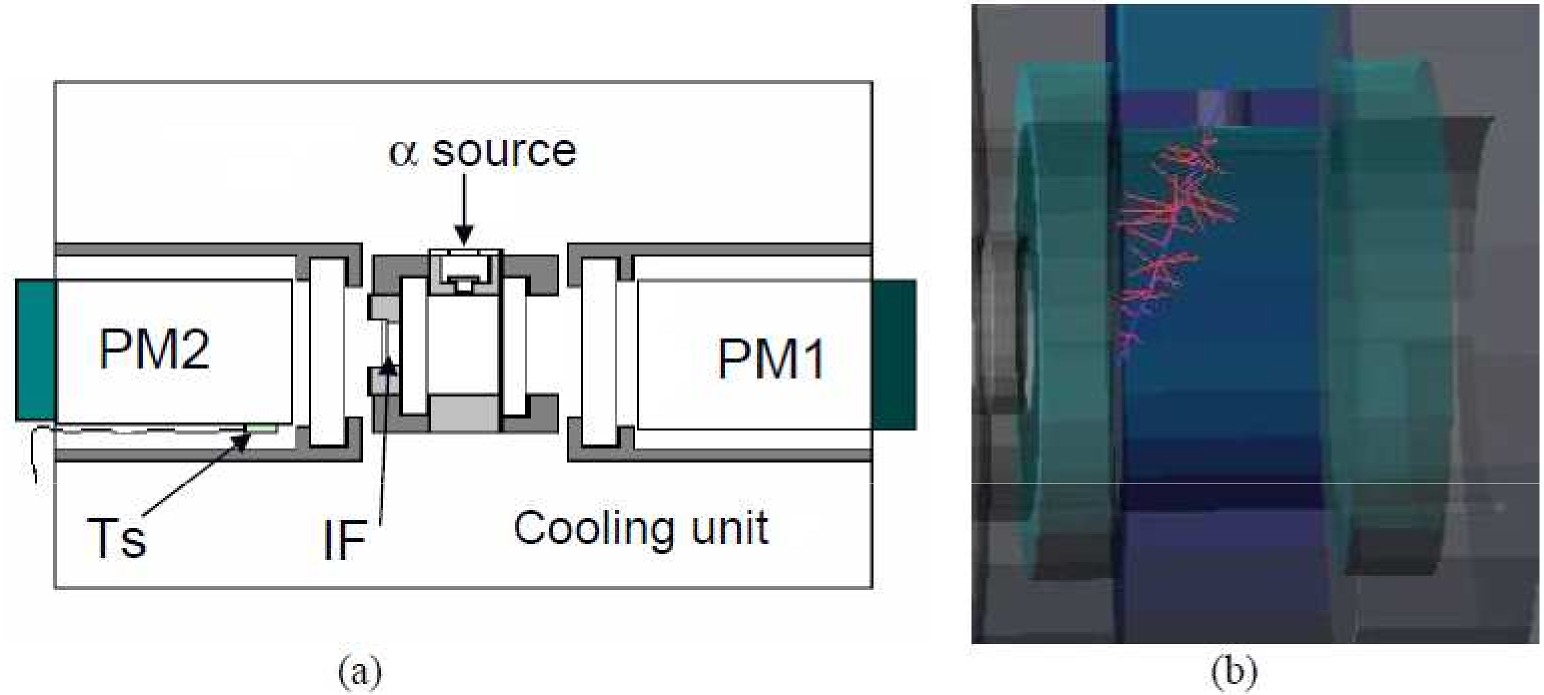
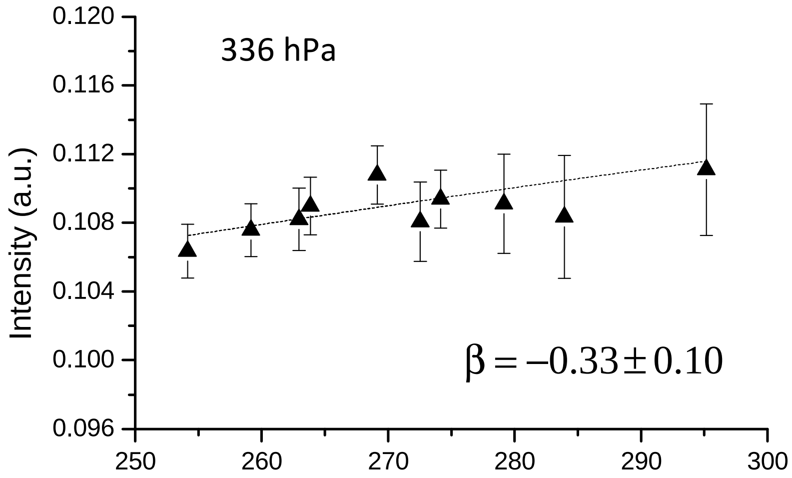
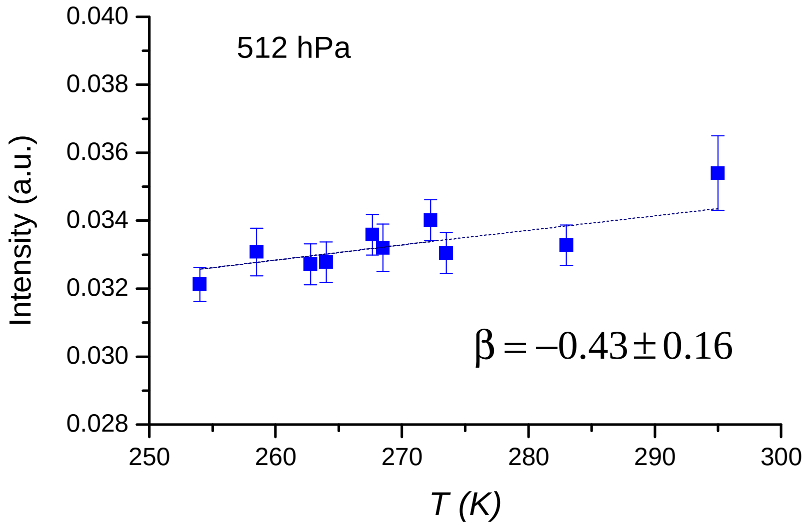
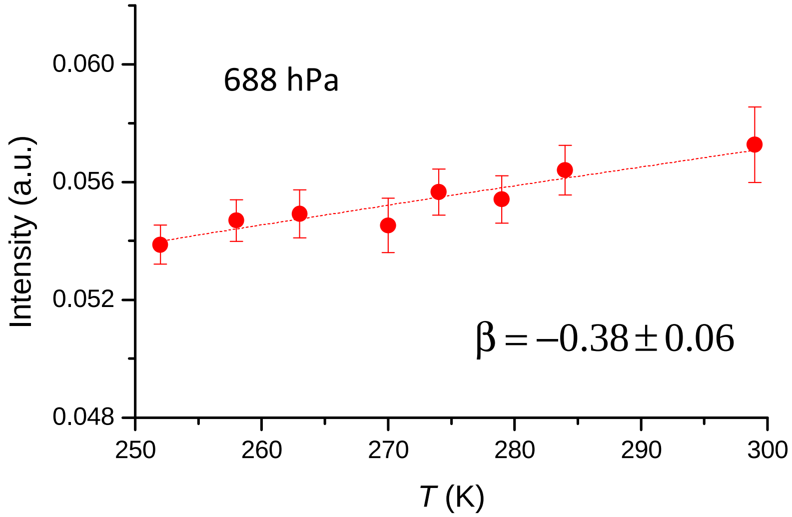


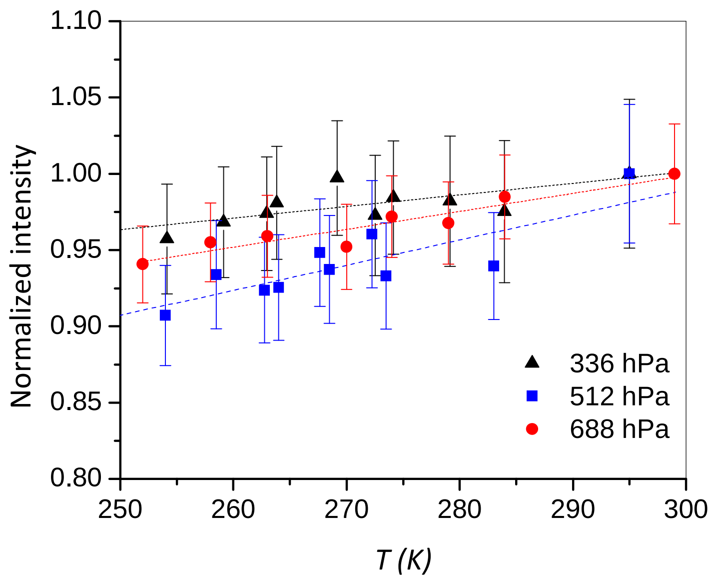
Fig. 1 – (a) Experimental set-up: PM1 and PM2 – photomultipliers; IF – interference filter centered at 340 nm; Ts – temperature sensor, PT100; (b) GEANT4 simulation of the set-up (@336 hPa, 290 K) showing one alpha track produced inside the gas cell (blue line) and the primary electron tracks (in red) (most electron are produced with very low energies and are stopped along the alpha track).

N2, 2P(0,0) band @ 337 nm





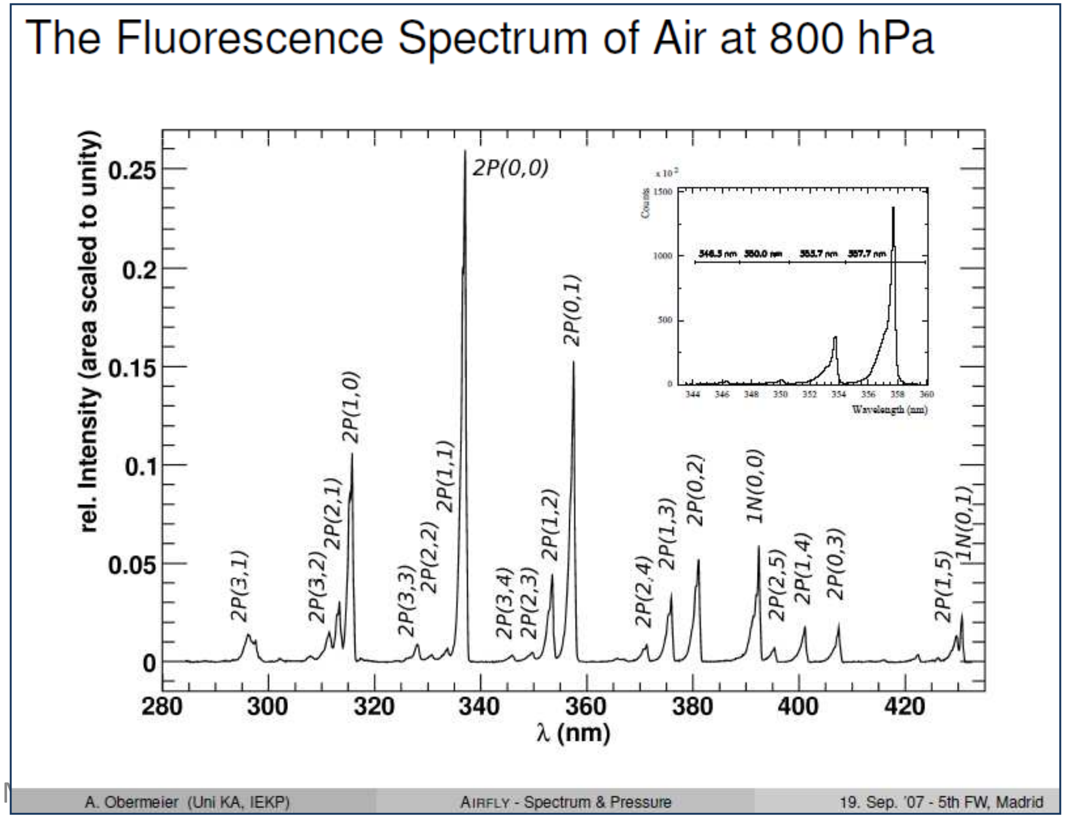




$$\overline{\beta}_0 = -0.37 \pm 0.07$$

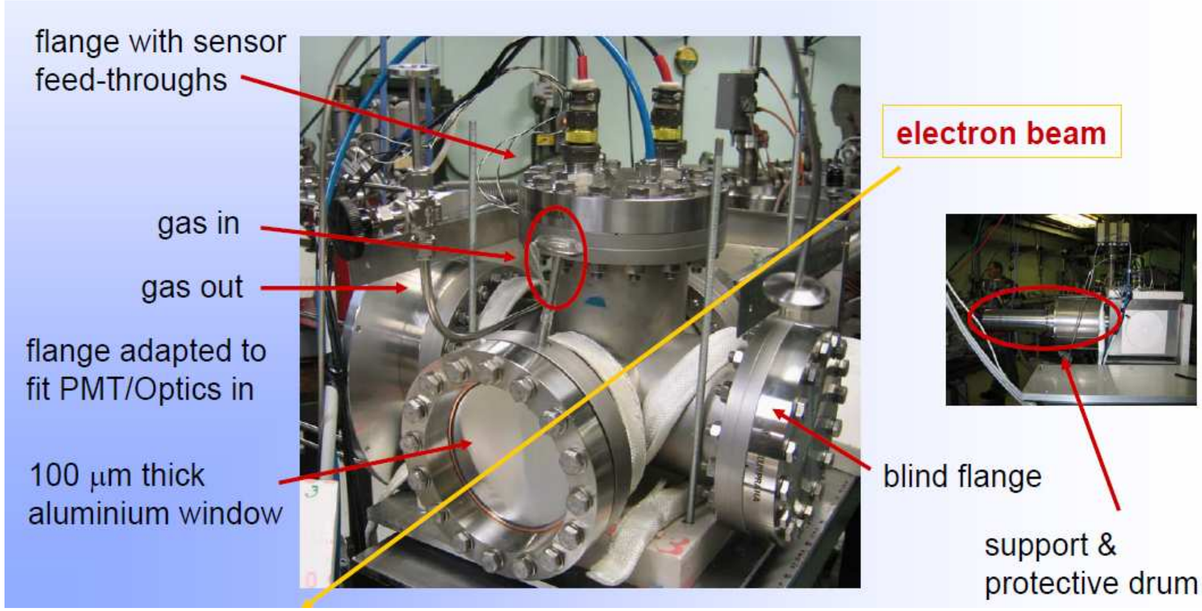
2) Light Yield measurements - AIRFLY collaboration (*M. Ave et al. NIM A597 (2008) 50, Nozka et al., Optik 120 (2009) 619*):

- Dry air @ ≈ 1000 hPa ;
- T = 240 K – 310 K @ constant gas density;
- Excitation source: 3 MeV electron VdG, DC beam, 10 μA
- Wavelengths : 284 – 429 nm using a spectrograph (ORIEL MS257) + CCD ;

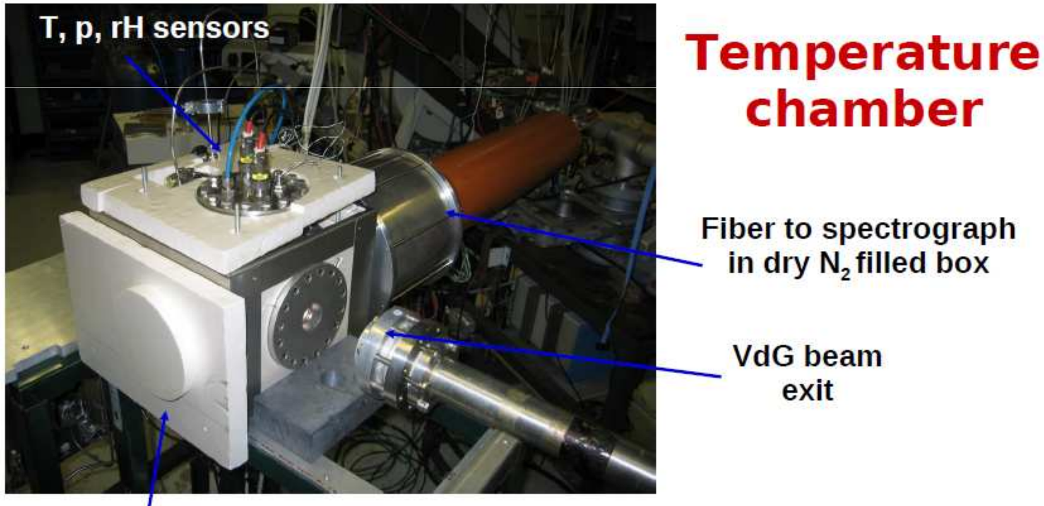


in A. Obermeier, 5th FW, El Escorial, Spain, Set. 2007

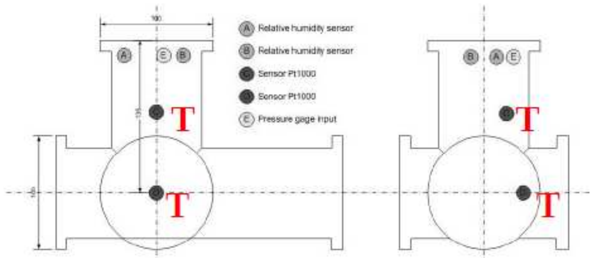
AIRFLY chamber used in the temperature dependence measurements.



in L. Nožka, 5th FW, Madrid, Set. 2007



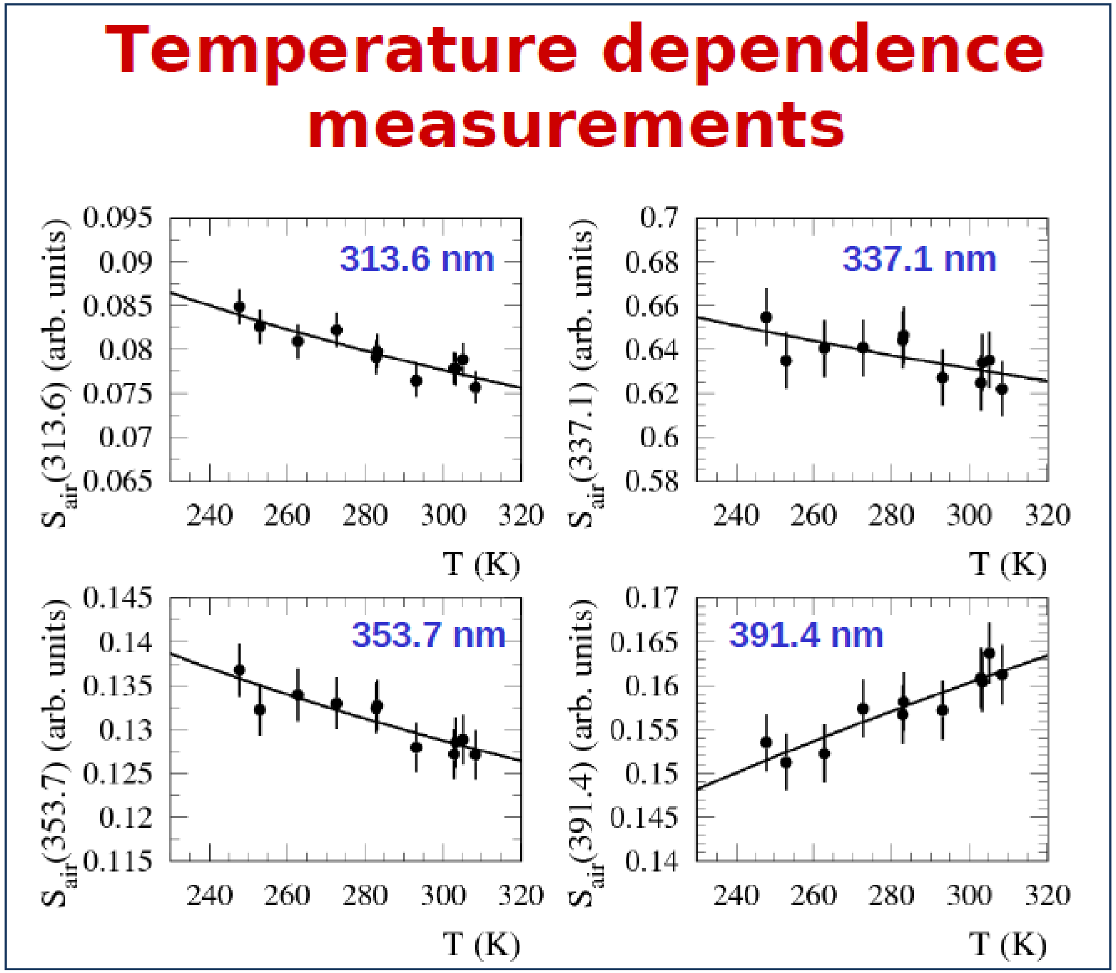
in M. Bohacova, 6th FW, L'Aquila, Italy, Feb. 2009



AIRFLY results:

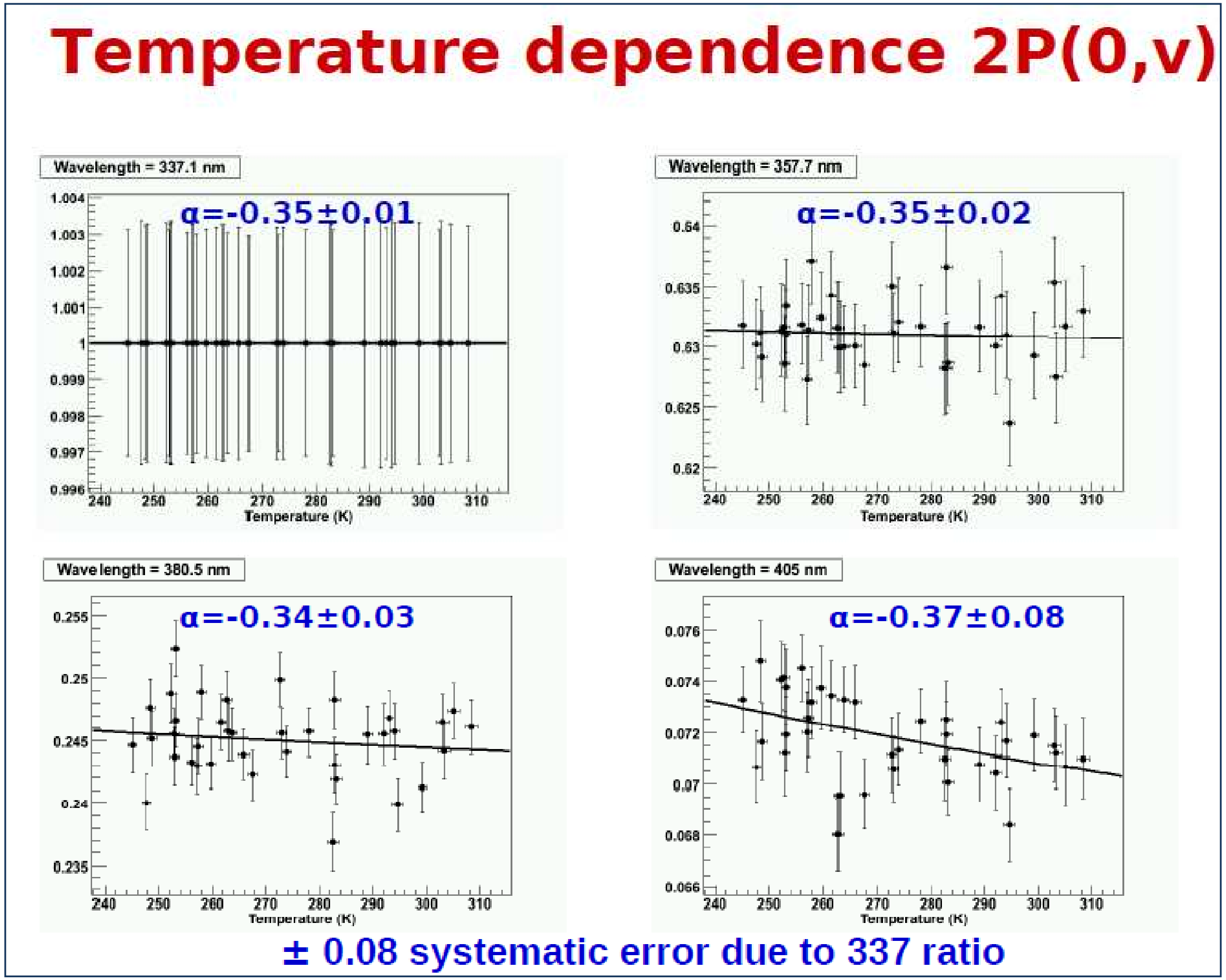
$$S_{v'v''}(p,T) \propto \frac{1}{1+\frac{p}{p'^{air}_{v'}(T_0)}\sqrt{\frac{T}{T_0}}\left(\frac{T_0}{T}\right)^{\alpha_\lambda}}$$

$$\frac{1}{p'_{air,v'}(T_0)} = \frac{f_{N2}}{p'_{N_2,v'}(T_0)} + \frac{f_{O2}}{p'_{O_2,v'}(T_0)}$$



in M. Bohacova, 6th FW, L'Aquila, Italy, Feb. 2009

$$\frac{S_{0v''}(p,T)}{S_{00}(p,T)} \ vs \ T$$



in M. Bohacova, 6th FW, L'Aquila, Italy, Feb. 2009

AIRFLY results for the measured temperature dependence parameters :

i) For some N_2 2P bands

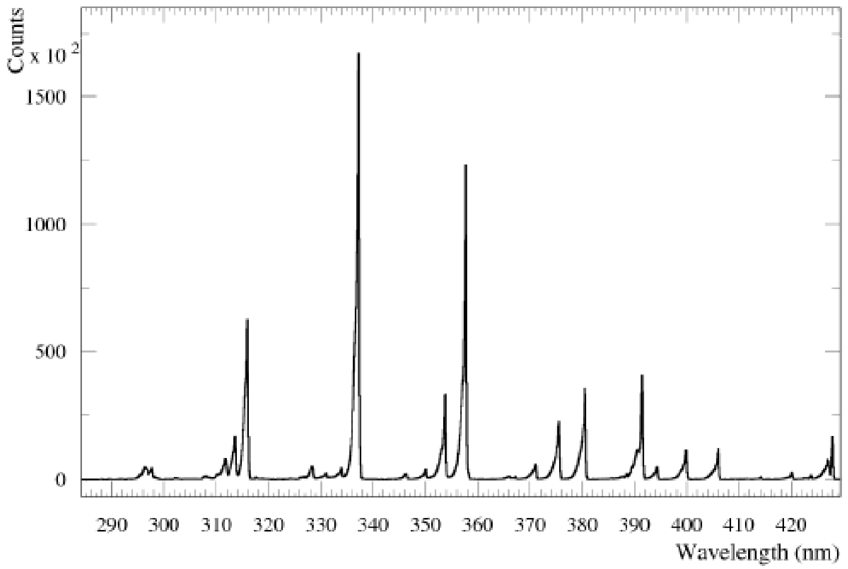
v’	(v’,v’’)	λ (nm)	α_λ [1]
0	(0,0)	337.1	-0.35±0.01
0	(0,1)	357.7	-0.35±0.02
0	(0,2)	380.5	-0.34±0.03
0	(0,3)	405.0	-0.37±0.08
1	(1,0)	315.9	-0.19±0.03
1	(1,2)	353.7	-0.22±0.04
1	(1,3)	375.6	-0.17±0.05
1	(1,4)	399.8	-0.20±0.08
2	(2,1)	313.6	-0.13±0.05
2	(2,3)	350.0	-0.38±0.16
2	(2,4)	371.1	-0.24±0.13
2	(2,5)	394.3	-0.20±0.14

± 0.08 systematic error due to 337 ratio

ii) For two N_2^+ 1N bands

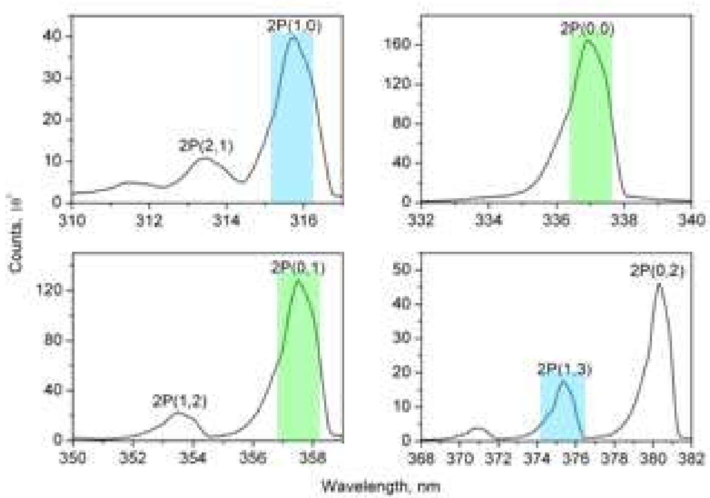
v’	v’’	λ (nm)	α_λ [1]
0	0	391.4	-0.79±0.03
0	1	427.8	-0.54±0.08

[1] ***M. Bohacova, 6th FW, L’Aquila, Italy, Feb. 2009***



3) Time resolved measurements @ TUM (*Pereira et al., Eur. Phys. J D 56 (2010) 325*)

- Excitation source: 10 keV electron-beam from an e-gun
- P = 50 hPa – 500 hPa
- T = 300 K to 210 K @ constant gas density;
- Pure N_2: (0,0), (0,1), (1,0) and (1,3) bands @ *337.1, 357.7, 315.9 and 375.5 nm* respectively , selected by a monochromator + PMT;
- Mixtures O_2/N_2 : (0,0) band @ *337.1 nm*



Emission bands of the N_2 2P system at 400 hPa (298 K). The wavelength resolution is 1 nm. *(Pereira et al., 6th AFWS, L' Aquila, Italy, Feb. 2009)*

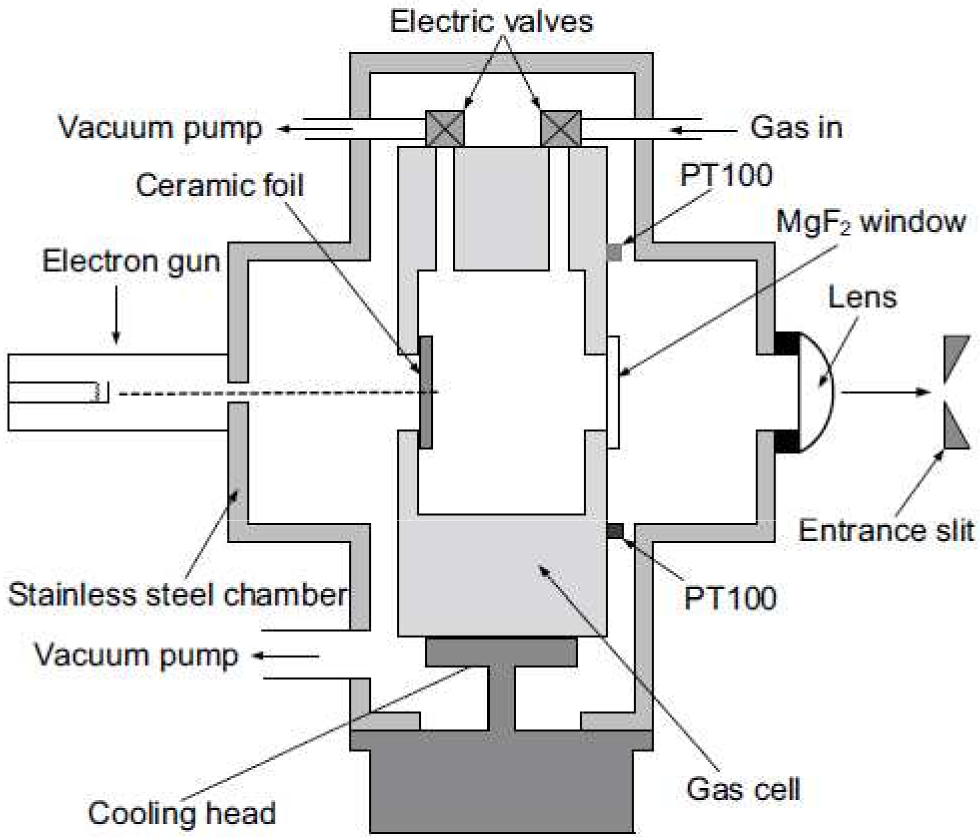
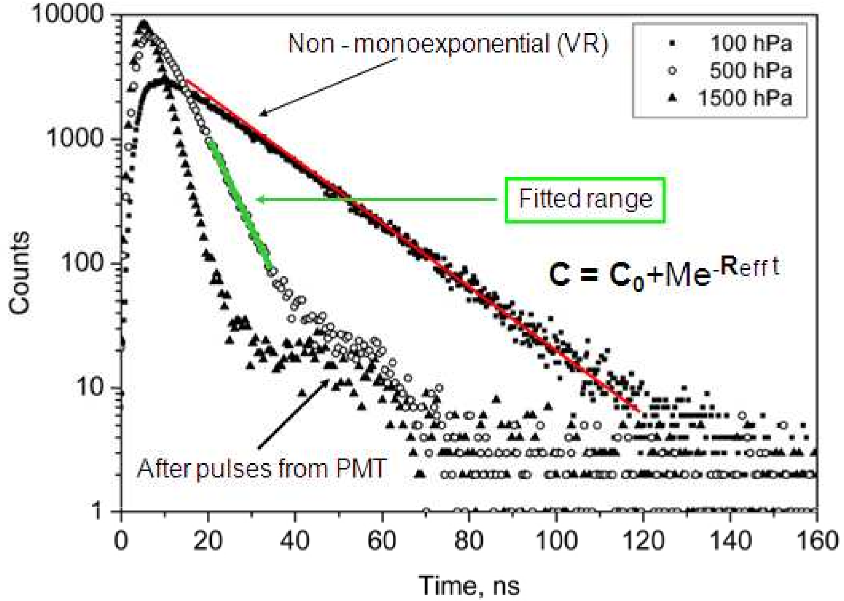


Fig. 1. Schematic drawing of the setup. From the detection system only the entrance slit of the monochromator is shown.

Pereira et al., Eur. Phys. J D 56 (2010) 325

Time spectra, 2P(0,0) [337,1 nm] in N_2



(Pereira et al., 6th AFWS, L' Aquila, Italy, Feb. 2009)

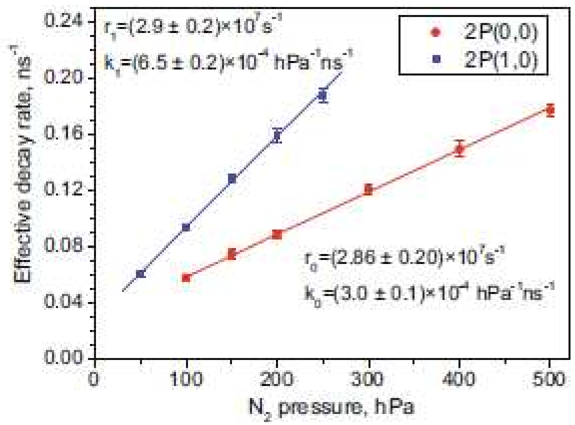


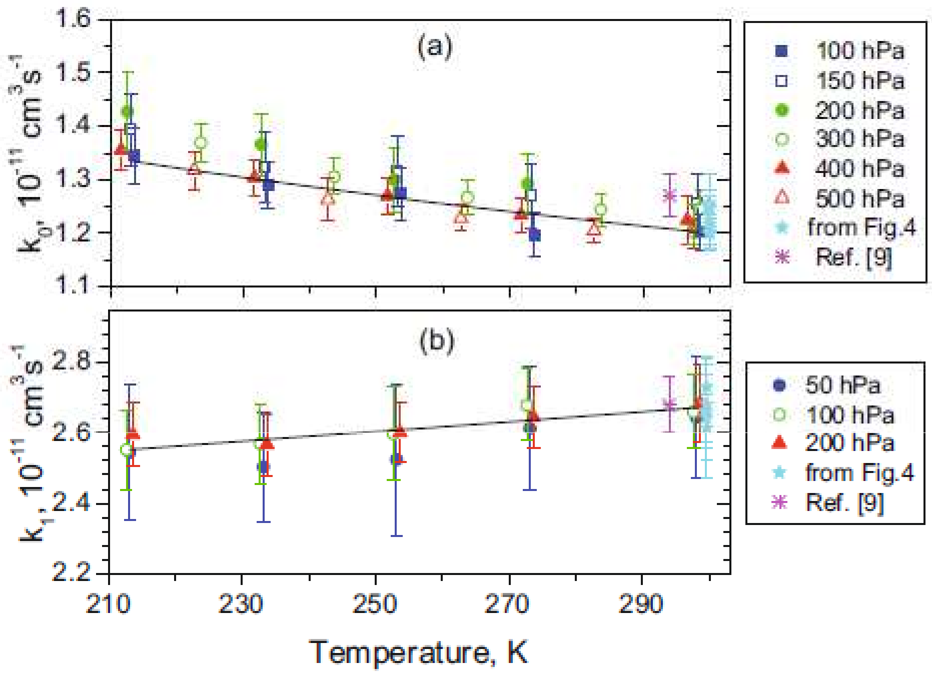
Fig. 4. (Color online) Effective decay rates of the vibrational levels $v' = 0, 1$ states as a function of nitrogen pressure measured at 298 K. Linear fits and the resulting quenching rate constants as well as radiative decay rates are shown for both vibrational levels.

$$k_{v',N2}(T) = \frac{R_{v'}(T) - A_{v'}}{N} \quad (cm^3 s^{-1})$$

$$\tau_1^0 = 34.5 \text{ ns}$$
$$\tau_0^0 = 35.0 \text{ ns}$$
$$k_0(298\ K) = (1.24 \pm 0.04) \times 10^{-11} \text{cm}^3\text{s}^{-1}$$
$$k_1(298\ K) = (2.60 \pm 0.08) \times 10^{-11} \text{cm}^3\text{s}^{-1}$$

Pereira et al., Eur. Phys. J D 56 (2010) 325

Temperature dependence of the quenching rate constants of N_2 (C,v'=0) and (C,v'=1) states by $N_2(X)$ molecules:



$$k_0(T) = C\left(\frac{T}{300}\right)^{\beta}$$

$$\beta_0 = -0.33 \pm 0.04$$

$$C = k_0(298K) = (1.2 \pm 0.2) \times 10^{-11} cm^3 s^{-1}$$

$$\beta_1 = 0.14 \pm 0.08$$

$$C = k_1(298K) = (2.67 \pm 0.14) \times 10^{-11} cm^3 s^{-1}$$

k_0 increases by (13±3)% from 300 to 210 K,

k_1 decreases by (5±3)% from 300 to 210 K

From $R_{v'}$ vs p, @ 298 K:

$$k_0(298\ K) = (1.24 \pm 0.04) \times 10^{-11} cm^3 s^{-1}$$

$$k_1(298\ K) = (2.60 \pm 0.08) \times 10^{-11} cm^3 s^{-1}$$

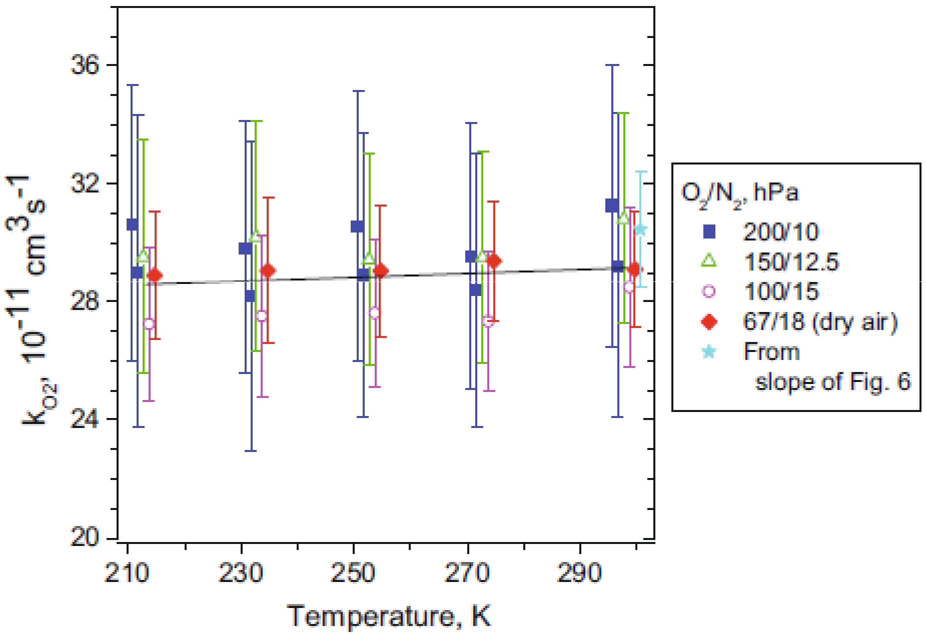
From intensity measurements:

$$\overline{\beta}_0^{LY} = -0.37 \pm 0.07$$

(Pereira et al., Eur. Phys. J D 56 (2010) 325)

Temperature dependence of the quenching rate constant of N_2 (C,v'=0) state by O_2:

$$k_{v',O2}(T) = \frac{R_{v'}(T) - A_{v'} - k_{v',N2}(T) N_{N2}}{N_{O2}} \quad (cm^3 s^{-1})$$



$$k_0(T) = C\left(\frac{T}{300}\right)^{\beta}$$

$$\beta_0 = 0.08 \pm 0.05$$

$$C = k_{0,O_2}(298K) = (29.5 \pm 3.0) \times 10^{-11} cm^3 s^{-1}$$

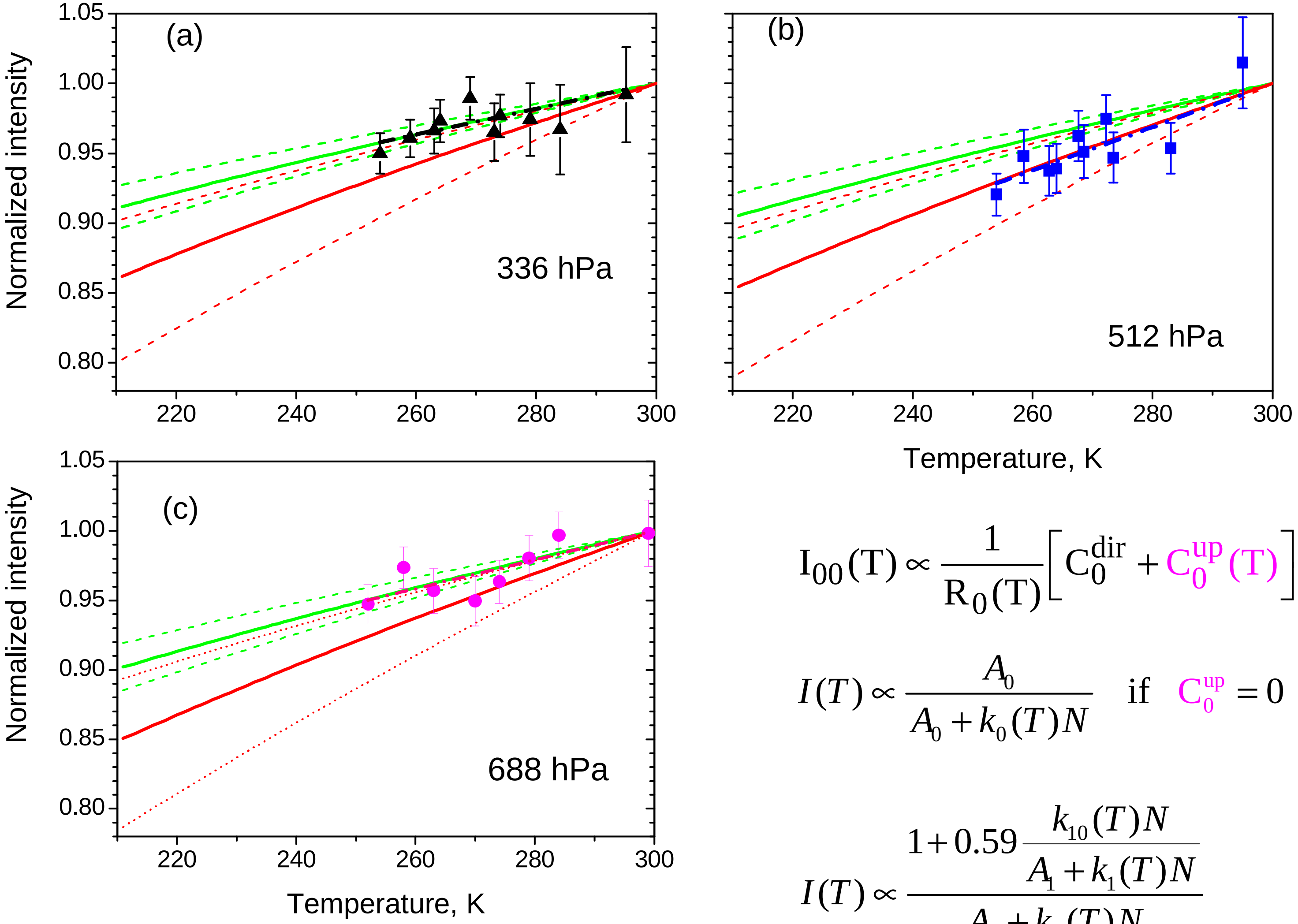
From $R_{0,O2}$ vs p_{O2}, @ 298 K:

$$k_{0,O_2}(298K) = (30.5 \pm 2.0) \times 10^{-11}\ cm^3\ s^{-1}$$

$k_{0,O2}$ decreases by (3±2)% from 300 to 210 K

Pereira et al., Eur. Phys. J D 56 (2010) 325

Comparison of Light Yield results and Time Resolved measurements – pure N_2



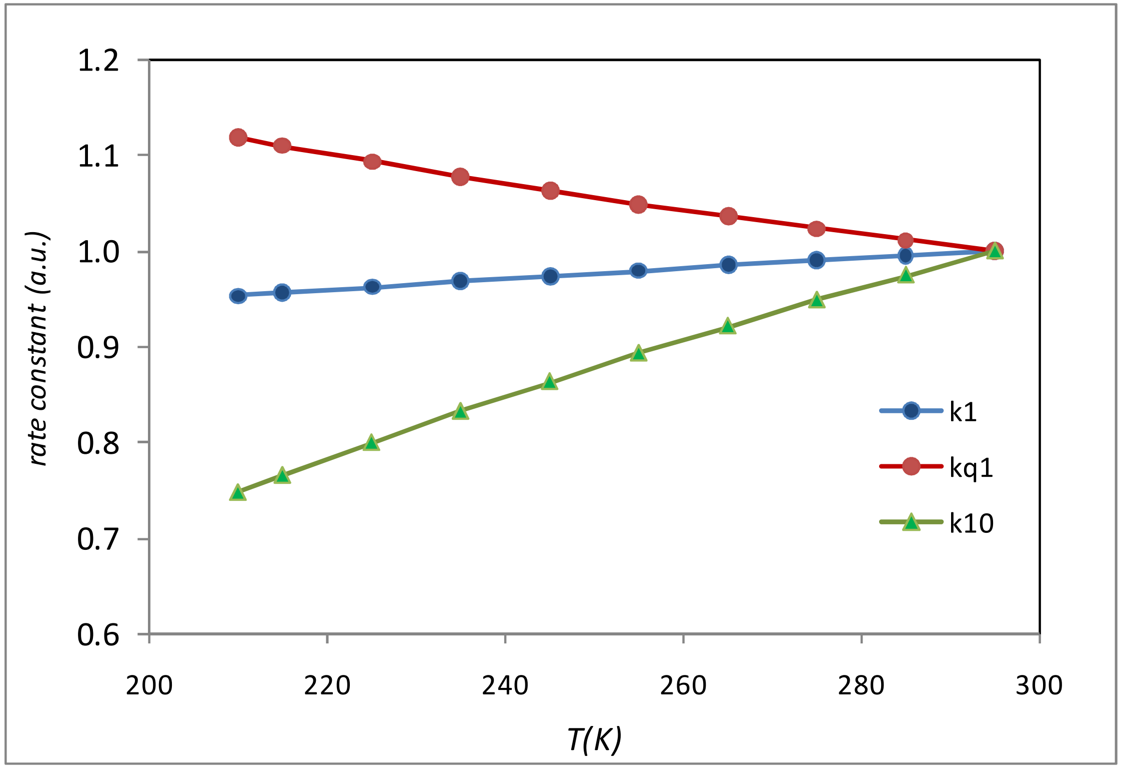
2P(0,0) band
λ = 337.1 nm

$$I_{00}(T) \propto \frac{1}{R_0(T)}\left[C_0^{dir} + C_0^{up}(T)\right]$$

$$I(T) \propto \frac{A_0}{A_0 + k_0(T)N} \quad \text{if} \quad C_0^{up} = 0$$ -> green lines

$$I(T) \propto \frac{1 + 0.59\dfrac{k_{10}(T)N}{A_1 + k_1(T)N}}{A_0 + k_0(T)N}$$ -> red lines

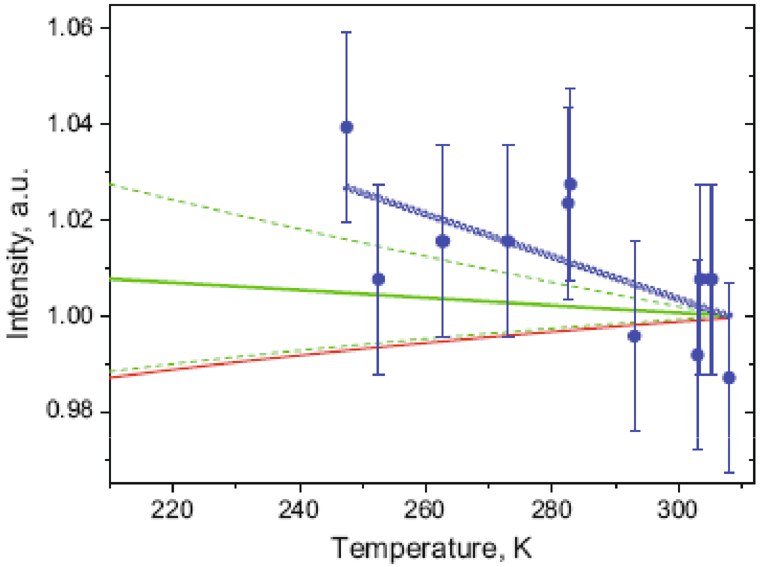
$$k_1(T) = k_{10}(T) + k_{q1}(T)$$



$$k_1(T) = k_{10}(T) + k_{q1}(T)$$

Comparison of Light Yield results from AIRFLY and Time Resolved Measurements – dry air:

2P(0,0) band, λ = 337.1 nm



Pereira et al., Eur. Phys. J D 56 (2010) 325

i) If VR is neglected ($C_0^{up} = 0$)

$$I(T) \propto \frac{A_0}{A_0 + k_{N_2}(T)N_{N_2} + k_{O_2}(T)N_{O_2}}.$$

-> green lines

ii) If vibrational relaxation is taken into account (red lines) ,

$$I(T) \propto \frac{1 + E_1 \frac{k_{10}(T)N}{R_1(T)}}{R_0(T)}; \quad \text{with}$$

$$\begin{cases} R_1(T) = A_1 + k_{1,N2}(T)N_{N2} + k_{1,O2}(T)N_{O2} \\ R_0(T) = A_0 + k_{0,N2}(T)N_{N2} + k_{0,O2}(T)N_{O2} \end{cases}$$

Monte Carlo simulation gives, $E_1 = \frac{C_1^{dir}}{C_0^{dir}} = 0.59$, just as in pure N_2.

$k_{1,N2}$ and $k_{1,O2}$ show a weak T dependence $\Rightarrow$ $R_1(T) \sim$ constant

Conclusions

- Quenching cross sections are temperature dependent;
- N_2 $C^3\Pi_u$ state:
  - the lowest vibracional state, v'=0, is the one that exhibits the strongest T dependence, both for the quenching by N_2 and O_2 molecules;
  - Temperature dependence of the quenching constant rates of vibrational states v'=1 and v'=2 (or of the intensities of the bands originating at v'=1 and v'=2) is weak and very similar;
- Quenching of N_2^+ (B,v'=0) state in pure nitrogen (α_λ=-0.82, according to *Belikov et al., J. Chem. Phys. 102 (1995) 2792*) and in dry air exhibits a strong dependence on T .
- Good agreement between the temperature dependence of the UV band intensities obtained by different techniques in different Labs.

Aspects that need further clarification:

- the different T dependences of (C, v'=0) and (C, v'=1,2) states

Still missing:

- The effect of humidity on the temperature dependence of air fluorescence band intensities;
- A theoretical explanation for the observed negative temperature dependence of the quenching cross section (*calculations are in progress*).