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Determination of $N_2(X)$ vibrational level populations and rotational temperatures using CARS in a D.C. low pressure discharge

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Résumé. — Pour la première fois, les populations vibrationnelles de l'azote dans l'état électronique fondamental ont été mesurées jusqu'à $v = 14$ dans une décharge continue à basse pression. Ces populations vibrationnelles ont été obtenues en enregistrant des spectres DRASC (Diffusion Raman Anti-Stokes Cohérente) des différentes bandes vibrationnelles de $N_2(X^1\Sigma_g^+)$ pour lesquelles la résolution spectrale de l'instrument permet de résoudre chaque raie rotationnelle. Dans la décharge, nous observons des distributions vibrationnelles hors équilibre de Boltzmann. Les paramètres vibrationnels sont compris entre 4 000 et 5 000 K, la température de rotation étant de l'ordre de 550 K. Des résultats similaires sont obtenus dans la post décharge où les populations vibrationnelles ont été mesurées jusqu'à $v = 10$. Les températures de rotation et de vibration sont alors respectivement 350 et 3 000 K. Les problèmes rencontrés au cours de l'enregistrement des spectres et la méthodologie suivie pour en déduire les populations sont discutés. Des comparaisons avec des modèles théoriques publiés par ailleurs sont aussi présentés.

Abstract. — For the first time, vibrational level population distributions of a low pressure D.C. flowing discharge were measured up to $v = 14$ using Coherent Anti-Stokes Raman Scattering (CARS). The vibrational populations of the ground state $N_2(X^1\Sigma_g^+, v)$ were obtained by recording rotationally resolved CARS spectra of the different vibrational bands. In the discharge region, the vibrational distributions have a non Boltzmann behaviour, as expected. The vibrational parameters were found to lie in the range 4 000-5 000 K, and rotational temperature to be about 550 K. Similar results were observed in the post-discharge region up to $v = 10$. The vibrational and rotational temperatures were about 3 000 and 350 K respectively. The problems experienced while recording CARS spectra in low density media are discussed and comparisons with previously published theoretical models are presented.

Introduction.

The understanding of the nitrogen vibrational kinetics in non-equilibrium media like gas discharges is of fundamental interest for plasma chemistry studies. $N_2(X, v)$ molecules are thought to play an important rôle during processes such as excitation, relaxation, ionization and dissociation [1]. Theoretical models have been developed to predict these vibrational distributions and their temporal evolution

(see for example [2-5]). However, these predictions were rarely compared to experimental results because optical dipolar transitions between the levels of the ground electronic state are forbidden, preventing the use of the relatively easy emission/absorption spectroscopies.

Several indirect measurement strategies have been proposed. Among them, we can mention the electron beam fluorescence diagnostics technique (EBFDT) used by Campbell [6] to investigate $N_2(X, v)$ up to $v = 5$ in the free jet expansion of a 100 mA, 2 torr, cooled electrical discharge. Jolly [7] has applied the Penning ionisation of N_2 by metast-

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able $\text{He}(2^3\text{S})$ to detect $\text{N}_2(X, v)$ ($0 \leq v \leq 7$) in the post-discharge region of an 80 mA, 5 torr continuous flowing discharge. More recently, Van Lonkhuyzen [8] has detected $\text{N}_2(X, v)$ for $v \leq 5$ with the photoelectron spectroscopy technique downstream of a microwave discharge.

However, direct observation of N_2 vibrational populations has now been made possible by the development of the Raman techniques.

The first use of CARS for the investigation of an N_2 discharge was reported by Shaub and coworkers [9]. These authors reported the non equilibrium distribution of $\text{N}_2(X, v)$ for $v \leq 7$ in a steady state, 4 mA, 10 torr discharge. In a similar discharge (7 mA, 12 torr), Smirnov [10] has observed $v \leq 6$. In a pulsed discharge, with a high current (~ 100 A) and a pressure of the order of 100 torr, Valyanski [11] and Devyatov [12] have measured $\text{N}_2(X, v)$ up to $v = 5$. From these experiments, they estimate the k_{01}^{10} rate to be about $10^{-13} \text{ cm}^3 \text{ s}^{-1}$, i.e. one order of magnitude smaller than the theoretical calculation of Billing [13]. Using spontaneous Raman scattering, Denisov and Akishev [14] have also measured the temporal evolution of high level populations ($v \leq 16$) in a 200 torr pulsed post discharge region.

In this paper, we present the result obtained by CARS in a flowing N_2 discharge at low pressure and for a current of 80 mA. We are able to measure the vibrational distribution up to the $v = 14$ level. The experimental procedure to obtain reliable populations and temperatures is fully described. We also report comparisons between our results and theoretical calculations.

1. Experimental set-up.

The flowing discharge is generated in a U-shaped tube with inner diameter of 2 cm (Fig. 1). Several nickel electrodes with an even spacing of 20 cm from each other, have been placed along the tube. Two of them are connected to the D.C. 10 kV supply which delivers a current of 80 mA. The nitrogen (purity $> 99.99\%$) flows through an M.F.A Eferel flowmeter and a liquid nitrogen trap and then from the anode to the cathode. The pressure is measured with a capacitive Datametrics gauge. Two conditions, 2 and 4 torr, have been studied. The flow rates are respectively $750 \text{ cm}^3 \text{ min}^{-1}$ and $1900 \text{ cm}^3 \text{ min}^{-1}$ (measured at standard temperature and pressure) and the velocities are 27 ms^{-1} and 36 ms^{-1} assuming that the static temperature is equal to the rotational temperature deduced from CARS measurements.

The probe CARS volume, i.e. the point where the CARS beams are focused, is located at the « bottom » of the « U » (see Fig. 1). To reduce the saturation effect [15], 500 or 710 mm focal length achromats are used. As a result, the optical ports

Fig. 1. — Diagram of the discharge tube. The figures along the pipe show the electrode positions. The results reported here have been obtained for the following conditions: — post-discharge region: electrodes # 4 and # 6, — discharge region: electrodes # 2 and # 4.

must be installed at the end of two long arms to reduce power density on the windows and so avoid optical damage.

The experimental arrangement allows the gas to be studied both within the discharge and in the post discharge region by connecting different selected electrodes to the power supply. In the same way, the transit time also can be varied.

The CARS beams are generated by the CARS laser assembly which is virtually identical to that described in [16]. Its main characteristics are as follows. The ω_1 pump beam is the frequency-doubled output of a single mode Nd-YAG chain. Its energy is 140 mJ per pulse and the pulse duration is 12 ns (repetition rate: 5 Hz). One third of this energy pumps a dye chain which emits the ω_2 Stokes beam. The dye laser spectrum consists of 4 or 5 longitudinal adjacent cavity modes, yielding a linewidth of 0.05 cm^{-1} (FWHM). The Stokes laser is tuned in steps of $5 \times 10^{-4} \text{ nm}$ between $\lambda \approx 607 \text{ nm}$ (for $v = 0$) and $\lambda \approx 590 \text{ nm}$ (for $v = 14$). The output energies are 80 and 3 mJ at ω_1 and ω_2 respectively; the beam diameters are 6 mm. Several optical arrangements can be selected for the present experiment.

2. Collinear beams or BOXCARS.

The collinear beam arrangement must be preferred to measure high vibrational state populations because its detectivity is one order of magnitude better than that of BOXCARS [17]. Also the saturation is expected to be reduced. However the probe volume

is not well defined and some signal is created in the side arms, i.e. far from the focal spot. Therefore, this arrangement is inappropriate if strong gradients can be present along the beam axis. As a consequence, the recording conditions have to be different for $v = 0$ and $v \gg 1$:

— for $v \gg 1$, a collinear beam arrangement is used since :

- i) no excited molecules are inside the side arms ;
- ii) no significant gradients are expected in the bottom of the « U » whether the discharge or the post discharge zones are analysed.

The actual probe volume extends from A to B in figure 1 over a length of the order of 10 cm ; its diameter is about 100 μm ;

— for $v = 0$, the BOXCARS arrangement is used lest this measurement be disturbed by the cold nitrogen filling the arms. Under our optical geometry (focal length of focusing optics : 500 or 710 mm ; beam diameters : 6 mm ; beam separation : 8 mm), the length of the probe volume (diameter $\sim 100 \mu\text{m}$), defined as the distance along which the entire anti-Stokes signal is created, is always less than 30 mm, i.e. short enough to prevent spurious signal from being created in the arms ;

— since the probe volume is different for the collinear beam and BOXCARS arrangements, these measurements are not directly comparable. Collinear beam results are rescaled to $v = 0$ BOXCARS spectra by a factor experimentally determined from the $v = 1$ to $v = 3$ vibrational bands, which can be accurately measured in both arrangements.

3. Parallel or crossed polarizations.

The CARS detectivity is limited by the fluctuations of the non resonant signal [18]. In this particular experiment, this signal is created :

- 1) By the remote resonances and the electronic non linearities of nitrogen.
- 2) By the windows (main contribution).

The crossed polarization arrangement is a well-known solution to cancel out this non resonant signal [19]. However it reduces the N_2 resonant signal by a factor close to 16 and, therefore its use is not always justified for diagnostics at low pressure. In order to avoid the use of crossed polarizations, some time was devoted to finding ways of reducing the non resonant signal prior to the final measurements. Using dichroic mirrors as windows (Fig. 2), it has been possible to reduce the non resonant contributions down to 20 photoelectrons per shot without a significant reduction of the resonant signal amplitude. Under these conditions, the arrangement with crossed polarizations is not useful, as was experimentally demonstrated on $v = 13$.

From the CARS bench, the ω_1 and ω_2 beams are directed to a reference cell filled with 600 torr of argon and then to the discharge tube (Fig. 3). The

Fig. 3. — Schematic diagram for the CARS experiment with referencing in cell C arranged « in series » with the signal channel. T : CARS table ; M_s : 530-680 nm broadband mirror ; M_{AS} : 410-535 nm broadband mirror ; D and D' : dichroic mirror ; F_1 - F_4 : lens ; S : double monochromator ; λ : Fizeau wavemeter.

Fig. 2. — Schematic diagram of the arrangement selected to reduce the non resonant signal generated in the windows.

CARS reference signal monitors signal fluctuations resulting from laser power instabilities and from changes in dye laser efficiency *versus* wavelength. Its role will be explained later. The reference and sample signals follow two identical channels; the anti-Stokes beams are separated from the pump beams by dichroic filters backed by a double monochromator. Then they are sent through an optical fiber to the phototubes housed in the electronics cabinet. After each laser pulses, signal and reference are digitized and their ratio is calculated by a PDP 11/23 computer. This ratio is averaged for 10 laser shots at each fixed Stokes position, then the computer increments the dye laser wavelength by one step. Between 200 and 600 dye laser positions are required for any particular vibrational band. Typical spectra are shown in figures 4 and 5.

Fig. 4. — Collinear beams CARS spectrum of $N_2(X, 3)$ in the 4 torr-80 mA discharge. Polarizations of ω_1 , ω_2 and ω_3 beams are parallel. Q lines are labelled by their J -numbers.

A wavemeter (Lasertechnics) monitors the Stokes wavelength while the spectrum is recorded. Reflected beams from the output window of the discharge cell (Fig. 2 and 3) are used for that purpose. The N_2 Raman line positions of high vibrational states which were found in this study will be published elsewhere.

Fig. 5. — Collinear beams CARS spectrum of $N_2(X, 13)$. Same discharge and CARS conditions as in figure 4.

4. Experimental procedure.

As is customary in CARS, information about the state of the molecular system is derived from lineshapes and line intensities. Spectra are recorded as a function of the frequency difference ($\omega_1 - \omega_2$). In the ideal case of monochromatic laser sources, the intensity recorded is proportional to the square of a nonlinear optical susceptibility, the resonances of the latter having an amplitude proportional to quantum state population differences [18]. When non-monochromatic lasers are used, the signal is given by a convolution integral. When the pump laser at ω_1 is monochromatic, the square root of the intensity S for an isolated Q line at ω_{vJ} is given by the simpler form [20]:

$$[S_{vJ}(\omega_1 - \omega_2)]^{1/2} = K_S(\omega_1, \omega_2) P_1 P_2^{1/2} \Delta N_{vJ} \sigma_v \times \left\{ \int_{\Gamma\omega_2} L(\omega_2) d\omega_2 \times \left[\int \frac{g(v_z) dv_z}{(\omega_1 - \omega_2) - \omega_{vJ} \left(1 - \frac{v_z}{c}\right) - i\Gamma_c} \right]^2 \right\}^{1/2} \quad (1)$$

where :

— ΔN_{vJ} is the population difference between (v, J) and $(v+1, J)$ states where v and J are the vibrational and rotational quantum numbers ;

— $K_S(\omega_1, \omega_2)$ is a factor which takes into account the optical transmission and the detector efficiency of the signal channel ;

— P_1 and P_2 are the pump and Stokes laser powers ;

— σ_v is the spontaneous Raman cross section ; σ_v in principle exhibits a weak J dependence, which is neglected here ;

— the expression inside the curly brackets represents the line profile. It is the convolution of the Stokes laser spectrum $L(\omega_2)$ with the isolated line profile ; in this expression the Doppler broadening is taken into account by the factor $\omega_{vJ} \frac{v_z}{c}$ where v_z is the projection of the velocity along the difference of wave vectors $(\mathbf{K}_1 - \mathbf{K}_2)$ and $g(v_z)$ is the Maxwell-Boltzmann velocity distribution function. Γ_c is the collisional broadening (HWHM).

Note that the N_2 lines are sharp and can be considered as isolated for $J \geq 6$ because of the low pressure in our experimental conditions.

To obtain reliable values for populations N_{vJ} from (1), a rather complex procedure must be followed. This is explained below.

4.1 SIGNAL NORMALISATION. — The CARS signal created in the reference cell is given by :

$$[R(\omega_1 - \omega_2)]^{1/2} = K_R(\omega_1, \omega_2) |X_{NR}| P_1 P_2^{1/2}. \quad (2)$$

$K_R(\omega_1, \omega_2)$ represents the efficiency of the reference channel. X_{NR} is the argon non resonant susceptibility which is independent of ω_1 and ω_2 .

For each laser shot, the ratio $P_3^{1/2} = [S(\omega_1, \omega_2)/R(\omega_1, \omega_2)]^{1/2}$ is therefore independent of laser power fluctuations. Pulse to pulse variations of $P_3^{1/2}$ are mainly caused by :

- i) fluctuations in the beam profiles and therefore in the beam overlap ;
- ii) shot noise ;
- iii) fluctuations in the longitudinal mode structure of the Stokes laser.

Causes i) and ii) can be evaluated by filling the discharge tube with argon (100 torr). The standard deviation σ of $P_3^{1/2}$ is then $\sim 2\%$. The shot noise contributes approximately one half of this figure. When N_2 spectra are recorded, cause iii) predominates at line centre positions. σ then increases to $\sim 20\%$.

Averaging several measurements (~ 10) for each spectral position, yields a better accuracy and smoother spectra.

The discussion below refers to averaged values of

$P_3^{1/2}$. As seen from (1) and (2), the proportionality factor K_S/K_R between $P_3^{1/2}$ and the population differences depends slightly on ω_1 and ω_2 because the signal and reference paths are separated and have wavelength-dependent transmissions. Wavelength variation of K_S/K_R is measured by recording a CARS spectrum with argon in the discharge tube.

4.2 ROTATIONAL TEMPERATURE. — The rotational temperature $T_R(v)$ of the vibrational band v is measured by plotting a Boltzmann diagram of the rotational line amplitudes $(S_{vJ}/R)^{1/2}$. The classical way would be to use the populations N_{vJ} . However, N_{vJ} can be replaced by $(S_{vJ}/R)^{1/2}$ because :

- i) the term inside brackets (expression (1)) is a constant ;
- ii) on the narrow spectral range of a vibrational band (~ 0.5 nm), K_S/K_R is nearly constant since the optical components of signal and reference channels are virtually identical. This is verified by recording a spectrum with the discharge tube filled with argon ;
- iii) the rotational temperature of two successive vibrational states are equal or, at least, very close. This can be checked *a posteriori*.

$T_R(v)$ is obtained from a linear regression with an accuracy ΔT_R . ΔT_R depends on :

- a) the number of rotational lines and the energy gap between the lower and the upper energy levels which have been probed ;
- b) the signal to noise ratio at peak intensity of each rotational line ;
- c) $T_R(v)$. A simple calculation shows that ΔT_R is proportional to $T_R^2(v)$ for fixed a) and b) conditions.

As a consequence, ΔT_R ranges generally from 10-50 K for low v and increases rapidly for high v .

Furthermore, it is interesting to compare ΔT_R with σ_T , standard deviation of repeated $T_R(v)$ measurements for any low v value and fixed discharge conditions. It is found that these two values are in good agreement.

4.3 FURTHER DATA PROCESSING TO OBTAIN VIBRATIONAL POPULATIONS. — To deduce the population difference densities

$$\Delta N_v = \sum_J (N_{v,J} - N_{v+1,J})$$

from the experimental data, we calculate $S_v^{1/2}$ where :

$$S_v^{1/2} = \sum_J \left(\frac{S_{vJ}}{R} \right)^{1/2} = \frac{1}{BF(T_R)} \left\{ \sum_{J=0}^{J_{\max}} (S_{vJ}/R)^{1/2} \right\} \quad (3)$$

where $BF(T_R)$ is the probability for an N_2 molecule to occupy the rotational states lower than or equal to

$J_{\max}$. $BF(T_R)$ is calculated assuming a Boltzmann distribution at T_R on the entire vibrational band.

As seen from (1) $S_v^{1/2}$ is proportional to ΔN_v , but the proportionality factor depends on v . We listed below the different terms of (1) which are v -dependent.

i) *Raman cross-section* σ_v . For an harmonic oscillator, σ_v is proportional to $(v+1)$. However, for high vibrational states, a Morse function is more adequate to represent the potential curve of N_2 [21]. The calculation [22] gives the following expression for σ_v :

$$\sigma_v = \sigma_0(v+1) f(v) \quad (4)$$

where σ_0 is the cross section for $v=0$ and $f(v)$ is a corrective term listed table I.

Table I. — *Corrective term $f(v)$ for the Raman cross section $\sigma(v)$ with $\sigma_v = \sigma_0(v+1) f(v)$.*

v	0	1	2	3	4	5	6	7
$f(v)$	1	1.01	1.03	1.04	1.05	1.07	1.08	1.09
v	8	9	10	11	12	13	16	
$f(v)$	1.11	1.12	1.14	1.15	1.17	1.18	1.20	

ii) *Line profile*. The line profile depends on v through the Doppler effect. We compare below the different broadenings:

- Γ_c being negligible [23], the lines of the non-linear optical susceptibility are predominately Doppler broadened (through $g(v_z)$ in (1)). The Doppler width $\Delta\omega_D$ is [20]:

$$\Delta\omega_D \text{ (cm}^{-1}\text{)} = 0.64 \times 10^{-6} \omega_v T^{1/2} M^{-1/2} \quad (\text{HWHM}) \quad (5)$$

where M is the mass number (g) and where the J dependence of ω_v (cm⁻¹) has been neglected. Assuming an equilibrium between translation and rotation at 540 K, the numerical application gives $\Delta\omega_D = 0.0065$ cm⁻¹ (HWHM) for N_2 ;

- the laser linewidth is: $\Gamma_{\omega_2} \approx 0.05$ cm⁻¹ (FWHM).

It is then clear that the primary source of line broadening is instrumental (Γ_{ω_2}). If the molecular resonances had identical width $\Delta\omega_D$, the spectral lines recorded would have the same shape; data processing would be facilitated and could be done without resorting to the numerical integration of (1). However, $\Delta\omega_D$ varies with the vibrational quantum number and temperature, causing changes in intensity. Nonetheless, the peak amplitude is easily

shown to be proportional to $\Delta\omega_D^{-1/2}$ because $\Gamma_{\omega_2} \gg \Delta\omega_D$.

Expressing $\Delta\omega_D$ in terms of (5) and comparing the line strength with that obtained for the calibration spectrum ($v=0$, $T=290$ K), $S_v^{1/2}$ has to be multiplied by the following correcting term:

$$\left[\frac{\omega_v}{\omega_0} \left(\frac{T_R}{290} \right)^{1/2} \right]^{1/2} \quad (6)$$

iii) *Residual saturation effect*. The stimulated Raman scattering (SRS) effect, which takes place along with CARS, induces population changes among the levels coupled by the Raman transition. This saturation is easily observed for plasma studies because the low pressure does not allow collisional rotational redistribution during the pulse duration. As a consequence, when we increase P_1 and P_2 , the signal is smaller than that estimated from (1).

Under our experimental conditions, saturation takes place. As it has been experimentally demonstrated, the phenomenon depends on the vibrational quantum number, but it has no effect on the rotational temperatures. This can be crudely explained by the fact that the Raman cross section does not depend on J , but is proportional to $(v+1)$.

To reliably calculate the populations, the CARS signal must be corrected for the saturation effect. For that purpose:

- the CARS signal was measured as a function of pump powers and for the first four vibrational states ($v \leq 3$);
- a numerical code solved the Bloch equations assuming Gaussian pulse shapes and single mode lasers, yielding CARS signals *versus* pump powers for $0 \leq v \leq 14$ [15];
- after proper rescaling of the pump powers to take into account the multimode structure of the Stokes laser, theoretical and experimental results are found to be in semi quantitative agreement for the first four v states;
- these theoretical predictions were then used to extrapolate the saturation effect on high vibrational states.

We introduce a corrective factor $s(v)$ which must be applied to the measurements in order to extract the exact number density differences from the saturated values (Table II).

iv) *Absolute number density* N_v . Using (1) and the different relations developed above, we find:

$$\Delta N_v = \Delta N_{0 \text{ cal}} \frac{S_v^{1/2}}{S_{0 \text{ cal}}^{1/2}} \left[\frac{\omega_v}{\omega_0} \left(\frac{T_R}{290} \right)^{1/2} \right]^{1/2} \times \frac{(K_S/K_R)_0}{(K_S/K_R)_v} \frac{1}{(v+1) f(v)} \frac{s(v)}{s(0)} \quad (7)$$

where $\Delta N_{0 \text{ cal}}$ is the number density of molecules

during a calibration experiment at 290 K and $S_{0\text{cal}}^{1/2}$ the corresponding CARS signal.

The vibrational distribution is then obtained from :

$$N_v = \sum_{v'=v}^{v_{\max}} \Delta N_{v'} + N_{v_{\max}+1} \quad (8)$$

where $v_{\max}$ is the quantum number of the upper measured level. To estimate $N_{v_{\max}+1}$, we introduce the parameter $\theta_{\max}$ representing the « temperature » between $v_{\max-1}$ and $v_{\max}$ ($\theta_{\max+1}$ is used for the pair $v_{\max}$ and $v_{\max+1}$). Neglecting the vibrational anhar-

Table II. — *Corrective factor $s(v)$ taking into account the saturation. $s(v)$ is deduced from a theoretical calculation scaled from experimental results obtained for $0 \leq v \leq 8$.*

v quantum number	$s(v)$ (a)	$s(v)$ (b)
0	1.05	1.28
1	1.09	1.45
2	1.14	1.63
3	1.19	1.81
4	1.24	2.00
5	1.28	2.18
6	1.33	2.35
7	1.38	2.51
8	1.42	2.66
9	1.47	2.80
10	1.52	2.94
11	1.56	
12	1.61	
13	1.66	
14	1.71	

(a) Calculation made to represent the experimental results recorded when the beams are focused with 710 mm focal length achromat.

(b) Calculation for the 500 mm focal length achromat case.

monicity, the condition $\theta_{\max} = \theta_{\max+1}$ leads to the following $N_{v_{\max}+1}$:

$$N_{v_{\max}+1} = \frac{(\Delta N_{v_{\max}})^2}{\Delta N_{v_{\max-1}} - \Delta N_{v_{\max}}} \quad (9)$$

The upper populations depend strongly on $N_{v_{\max}+1}$ and therefore on the assumption made for $\theta_{\max}$ and $\theta_{\max+1}$. To illustrate this point, we present the distributions obtained for two conditions namely

$$\theta_{\max} = 1.10 \times \theta_{\max+1}$$

and

$$\theta_{\max} = 0.9 \times \theta_{\max+1}.$$

$N_{v_{\max}+1}$ is then given by (see Appendix A)

$$N_{v_{\max}+1} = \frac{(\Delta N_{v_{\max}})^2}{\Delta N_{v_{\max-1}}(1 - \varepsilon) - \Delta N_{v_{\max}}(1 + \varepsilon) - \varepsilon N_{v_{\max}+1}^0} \quad (10)$$

where $N_{v_{\max}+1}^0$ is calculated from (9) and :

$$\varepsilon = [\omega_e - 2 \omega_e x_e v_{\max}] \frac{hc}{k} \frac{\theta_{\max+1} - \theta_{\max}}{\theta_{\max} \theta_{\max+1}} \quad (11)$$

using the common notations of [24] in cm^{-1} .

To get an empirical estimate of the ΔN_v and N_v uncertainties, data recorded on different days for identical conditions have been compared. The standard deviation is 3 % for $\Delta N_{v=1}$ and 10 % for $\Delta N_{v \approx 10}$.

Pointing out that N_v is obtained by adding successive and uncorrelated ΔN_v , we find that the N_v uncertainty ranges from 3 % for $v = 0$ to 5 % for $v = 10$.

5. Results and discussion.

The figures 6 and 7 give the results for a pressure of 2 torr and a discharge current of 80 mA (see Fig. 1 for the discharge geometries).

Concerning the data in figure 6, the probe volume is in the discharge region, at time $t = 11$ ms downstream from the anode, as calculated from $t = l/\langle v \rangle$ where l is the distance from the anode to the probe volume ($l = 40$ cm) and $\langle v \rangle$ the averaged velocity deduced from the mass flow rate, the rotational temperature, and the pressure. Figure 6a shows a slight increase of $T_R(v)$ versus v , and a large increase of ΔT_R with the higher values of v . While we do not consider the increase of $T_R(v)$ to be significant in view of the measurement uncertainties, possible causes for the phenomenon could be :

- poor signal/background ratio at high v ;
- differential pumping of the higher J states similar to the anharmonic pumping of Treanor [2].

a)

b)

Fig. 6. — 2 torr, 80 mA current discharge region : a) rotational temperature for each vibrational band ; b) vibrational populations : — experimental results for 3 different $N_{v=12}$ population estimates (see text) ; --- Treanor Gordiets model ; • : M. Capitelli et C. Gorse calculation for 10 ms residence time ; + same calculation for 20 ms residence time.

Note that, for some v values, several measurements have been repeated. The average and standard deviation of $T_R(v)$ for the first 10 vibrational levels is $T_R = 530 \pm 30$ K.

The vibrational parameter θ_1 , calculated from the ratio between $v = 1$ and $v = 0$ populations, is $5\,300\text{ K} \pm 350\text{ K}$ where the accuracy reflects the 5 % uncertainty on the ratio of the $v = 0$ and $v = 1$ populations.

a)

b)

Fig. 7. — 2 torr, 80 mA current post discharge region : a) rotational temperature ; b) vibrational populations : experimental results for 3 different $N_{v=11}$ estimates (see text) ; --- Treanor Gordiets model.

The populations of figure 6b weakly depend on the assumption made for $N_{v=12}$, and whatever this assumption, the distribution never has a Boltzmann-like behaviour.

The conditions of figure 7 are as follow : the probe volume is in the post discharge region, 15 ms downstream of the cathode ; the residence time in the discharge also is 15 ms.

The average value and standard deviation of $T_R(v)$ (Fig. 7a) are $T_R = 340 \text{ K} \pm 22 \text{ K}$. The vibrational parameter θ_1 is $3\,350 \text{ K} \pm 150 \text{ K}$ (Fig. 7b).

The same discharge is also studied for a pressure of 4 torr. The residence time to the probe volume is now 8 ms. Results are similar to the 2 torr discharge. However, the rotational temperatures are more accurate because populations of higher rotational states have been measured (Fig. 8a). A very small variation of the rotational temperature as a function of v is also observed. A rotational temperature T_R can still be defined as the average of $T_R(v)$. From the first 10 vibrational states we get $540 \text{ K} \pm 30 \text{ K}$. The vibrational parameter θ_1 associated with the population distribution of figure 8b is $4\,000 \text{ K} \pm 200 \text{ K}$.

Fig. 8. — 4 torr, 80 mA current discharge region : a) rotational temperature ; b) vibrational populations : — experimental results for 3 different $N_{v=15}$ estimates (see text) ; --- Treanor Gordiets model ; • H. Bruner calculation.

These experimental distributions are then compared with numerical results predicted by the analytical Treanor Gordiets model [2] : it gives the $N_2(X, v)$ steady state distribution taking into account only V-V and V-T transfers. The computed $N_2(X, v)$ distribution depends on two parameters, namely T_R and θ_1 , which are determined experimentally. The theoretical formula is simplified as in [7].

At 2 torr (Figs. 6b and 7b), a discrepancy is observed for the high v states both in the discharge and in the post discharge regions : the experimental $N_2(X, v)$ for $v \geq 6$ are always below the computed values. Two explanations can be suggested :

- i) the wall deactivation becomes comparable to V-V transfer rates ;
- ii) the steady state distribution, as calculated by the Treanor Gordiets model, is not reached.

However, it is very difficult to estimate the relative importance of these two points. For example, if we are able to compare the wall deactivation frequency ν_w and V-V transfer frequency ν_{v-v} for $v = 1$ (following Massabieaux [25], Billing [13] and experimental results of Black [26]), results and estimates are missing for higher v states. Increasing the pressure also does not allow us to choose among the two possible explanations. As observed in figure 8b, the agreement is improved ; this could be due to :

- 1) the V-V transfer frequency increases and becomes dominant over wall deactivation, which remains constant ;
- 2) the steady state is approached sooner since V-V transfer rates are greater.

In figure 6b, we have also shown a theoretical distribution computed by M. Capitelli and C. Gorse for our experimental conditions. The input parameters are : $T_R = 500 \text{ K}$, $E/N = 5.5 \times 10^{-6} \text{ V cm}^2$, $n_e = 1.7 \times 10^{10} \text{ cm}^{-3}$ and $P = 2 \text{ torr}$. The temporal behaviour of the vibrational distribution is calculated at 10 ms and 20 ms [3]. The best agreement is obtained for the 20 ms case, although the residence time was estimated to be close to 11 ms. Discharge geometry and uncertainties in the n_e determination are two possible explanations for the slight discrepancy. In addition, the model represents the growth of vibrational populations as a function of time (not as a function of position) and assumes that the input parameters remain constant and equal to their initial values during the calculation.

This calculation, which is close to the present CARS measurements, is important for two reasons :

- it shows that the steady state distribution is not reached after 10 ms. The $N_2(X, v = 11)$ population change between 10 ms and 20 ms is comparable with the mismatch observed between experimental and Treanor Gordiets results ;

— even though the calculation did not take into account wall deactivation, the computed distribution is closer to experimental results than numerical values given by the Treanor Gordiets model.

As a consequence of the above discussion, the discrepancy found with the Treanor Gordiets model is probably caused by the fact that steady state is not reached.

A theoretical distribution predicted by the model of Brunet *et al.* [4] is also compared with our experimental results. The model calculates the vibrational distribution and the rotational temperature as a function of the distance from the anode. The input parameters are the discharge current, the gas flow velocity, the pressure and the radius of the discharge tube. The calculations have been made assuming no radial profile for the various parameters (one dimensional model) in order to reduce the computation time of the program. The overall agreement for $N_2(X, v)$ is very good (Fig. 7b). Moreover, the rotational temperature found in the calculation is 515 K, i.e. very close to the experimental value of 520 K. According to Brunet [27], the vibrational distribution found could be slightly different with a more realistic two-dimensional model.

Conclusion.

For the first time, the $N_2(X, v)$ distribution is measured in a D.C. discharge at low pressure up to $v = 14$. These results are due to the good detectivity of CARS which proves to be a powerful and reliable apparatus for plasma studies [28].

The same kind of non-Boltzmann distributions are observed in this work and in previous papers published by Campbell [6] and Jolly [7]. The observed distributions agree rather well with Treanor-Gordiet's calculations for $v \leq 5$. Further, more sophisticated numerical models yield even better agreement.

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Appendix A. Extrapolation of $N_{v_{\max}+1}$ from the measurements of $\Delta N_{v_{\max}}$ and $\Delta N_{v_{\max}-1}$.

We assume :

$$\begin{aligned} N_{v_{\max}} &= N_{v_{\max}-1} \exp[-(\omega_e - 2\omega_e x_e v_{\max}) hc/k\theta_{\max}] = N_{v_{\max}-1} \exp(-a/\theta_{\max}) \\ N_{v_{\max}+1} &= N_{v_{\max}} \exp[-(\omega_e - 2\omega_e x_e (v_{\max} + 1)) hc/k\theta_{\max+1}] = N_{v_{\max}} \exp(-a'/\theta_{\max+1}). \end{aligned}$$

So,

$$\begin{aligned} \Delta N_{v_{\max}} &= N_{v_{\max}} - N_{v_{\max}+1} = N_{v_{\max}-1} \exp(-a/\theta_{\max}) - N_{v_{\max}} \exp(-a'/\theta_{\max+1}) \\ &= N_{v_{\max}-1} [\exp(-a'/\theta_{\max+1})]^{\frac{\theta_{\max+1}}{\theta_{\max}} \frac{a}{a'}} - N_{v_{\max}} \exp(-a'/\theta_{\max+1}). \end{aligned}$$

We can observe that $a - a' = 2\omega_e x_e \ll a, a'$.

So we can consider that $a = a'$, and by developing the first term of the right hand side :

$$[\exp(-a/\theta_{\max+1})]^{\frac{\theta_{\max+1}}{\theta_{\max}}} = [\exp(-a/\theta_{\max+1})] \left[1 - (a/\theta_{\max+1}) \frac{\theta_{\max+1} - \theta_{\max}}{\theta_{\max}} \right].$$

We obtain :

$$\begin{aligned} \Delta N_{v_{\max}} &= (N_{v_{\max}-1} - N_{v_{\max}}) \exp(-a/\theta_{\max+1}) - N_{v_{\max}-1} (a/\theta_{\max+1}) \frac{\theta_{\max+1} - \theta_{\max}}{\theta_{\max}} \exp(-a/\theta_{\max+1}) \\ &= \left[\Delta N_{v_{\max}-1} - N_{v_{\max}-1} (a/\theta_{\max+1}) \frac{\theta_{\max+1} - \theta_{\max}}{\theta_{\max}} \right] \exp(-a/\theta_{\max+1}). \end{aligned}$$

Then :

$$\begin{aligned} \frac{N_{v_{\max}+1}}{\Delta N_{v_{\max}}} &= \frac{N_{v_{\max}}}{\Delta N_{v_{\max}-1} - \varepsilon N_{v_{\max}-1}} = \frac{\Delta N_{v_{\max}}}{\Delta N_{v_{\max}-1} - \Delta N_{v_{\max}} - \varepsilon N_{v_{\max}-1}} = \\ &= \frac{\Delta N_{v_{\max}}}{\Delta N_{v_{\max}-1}(1 - \varepsilon) - \Delta N_{v_{\max}}(1 + \varepsilon) - \varepsilon N_{v_{\max}+1}}. \end{aligned}$$

To obtain equation (10), $\varepsilon N_{v_{\max}+1}$ is replaced by $\varepsilon N_{v_{\max}+1}^0$ where $\varepsilon N_{v_{\max}+1}^0$ is the value for $\varepsilon = 0$.

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