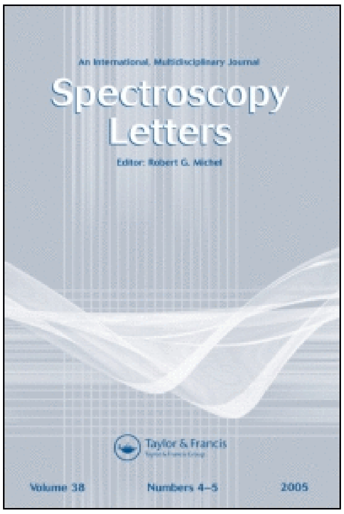

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Measurement of Rotational Temperature by Simulated Molecular Spectra

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MEASUREMENT OF ROTATIONAL TEMPERATURE BY SIMULATED MOLECULAR SPECTRA.

KEY WORDS : Emission Spectroscopy, Rotational Temperature, Molecular Spectra, Calculated Spectra, Thermal Plasma.

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ABSTRACT

The measurement of temperature of heavy particles in a thermal plasma is based on the comparison of experimental rotational spectrum obtained by optical emission spectroscopy and synthetic spectra calculated for different temperatures. The calculation principle of the synthetic spectra is detailed as well as the temperature accuracy obtained. This method is used to measure the temperature of an Ar-CO_2 mixture plasma produced in a wall stabilized arc with molecular spectra of C_2 (Swan system) and CN (violet system).

I INTRODUCTION

Most plasmas present a desequilibrium between the electronic temperature and the temperature of heavy particles. This desequilibrium is a fundamental parameter in the calculations of plasma composition because it affects the reactions occurring between chemical species [1,2]. The electronic temperature can be determined by probe measurement [3] or Stark broadening of hydrogen H_β line [4]. Molecular spectroscopy allows the determination of rotational temperature. The rotational temperature of ground states or metastable states has been determined by laser induced fluorescence (LIF) on CO molecule [5,6], CCl [7], C_2 [8], CN [9,10], CH [11] radicals, Cl_2^+ ion [12] or the optogalvanic effect [13]. The rotational spectrum of SiN radical has been recorded in an RF reactor at 13.56 MHz with silicium in a nitrogen plasma [14]. The rotational temperature of molecular excited states has been studied in the last few years. The rotational temperature, in a nitrogen arc at atmospheric pressure, has been measured [15] using high resolution spectroscopy. In an arc jet, at low pressure, the rotational temperature has been measured using optical spectroscopy combined with the calculation of synthetic spectra of the first positive system of nitrogen [16] and NH radical [17].

The aim of this work is to define the principle of the measurement of rotational temperature in an Ar-CO_2 mixture thermal plasma at atmospheric pressure. This measurement is based on the comparison of the experimental rotational spectrum obtained by optical emission spectroscopy and the synthetic spectra calculated for different temperatures. The calculation principle of the synthetic spectra is detailed as well as the temperature accuracy obtained.

II PRINCIPLE OF TEMPERATURE MEASUREMENT

In a gas discharge plasma in mixture of CO_2 with inert gas (Ar), a molecular carbon formation process occurs, characterised by the Swan band $C_2(d^3\Pi_g) \rightarrow C_2(a^3\Pi_u)$, located in the visible region of the spectrum [18]. The violet system $CN(B^2\Sigma^+) \rightarrow CN(X^2\Sigma^+)$ of the CN radical has also been observed [19]. These two bands are the most intense ones observed in the visible and near UV range.

The determination of gas temperature in the arc is performed by measurements of the rotational temperature of the C_2 and CN radicals. Owing to a small energy separation between the rotational levels of the molecules, the populations of the rotational states correspond more closely to the translational gas temperature in the arc column. Inelastic electron-molecule collisions excite the C_2 and CN radicals without altering their angular momentum. Hence the excited states have the same rotational distribution as the ground state. The $C_2(d^3\Pi_g)$ lifetime of the order of 1 μs [20], and the $CN(B^2\Sigma^+)$ lifetime of the order of 60 ns [21,22] are much longer than the mean time between collisions at the atmospheric pressure, which can be evaluated less than 1 ns. Since rotational equilibrium typically requires ≈ 10 collisions, rotation-translation equilibrium does prevail for all emitting species. Hence the excited states $C_2(d^3\Pi_g)$ and $CN(B^2\Sigma^+)$ have the same rotational distribution as the ground states, respectively $C_2(X^1\Sigma_g^+)$ and $CN(X^2\Sigma^+)$. Boltzmann's law for these molecule populations is therefore valid.

Calculated Spectra

The following relation may be written for the intensity of each rotational line emitted [23] :

$$I_{e''v''J''}^{e'v'J'} = D(J')\,\nu^4 \exp\left(\frac{\left(F_v(J') - F_v(0)\right) hc}{kT_{rot}} \right)$$

where D(J') is a spectroscopical function taking into account the strength line [24], the strength band and the rotational partition function, ν the transition frequency, k the Boltzmann constant, h the Plank constant, c the light velocity, T_{rot} the rotational temperature and $F_v(J')$ the rotational energy of the upper level J'. The total energy of the molecule is the sum of the electronic, vibrational and rotational energy [23].

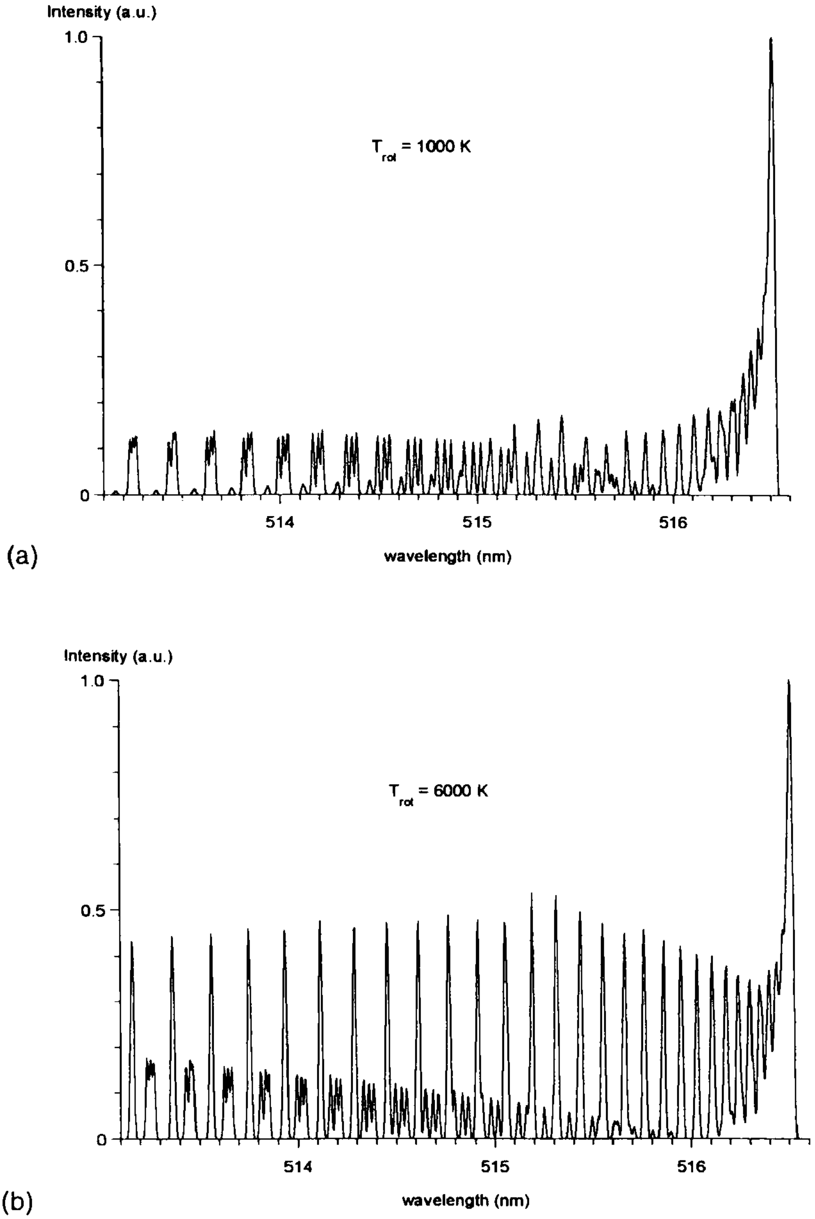

FIG. 1 : Simulated spectra : Swan system of C_2, (0-0) band, FWHM = 0.014 nm. a) T_{rot} = 1000 K. b) T_{rot} = 6000 K. c) T_{rot} = 12000 K.

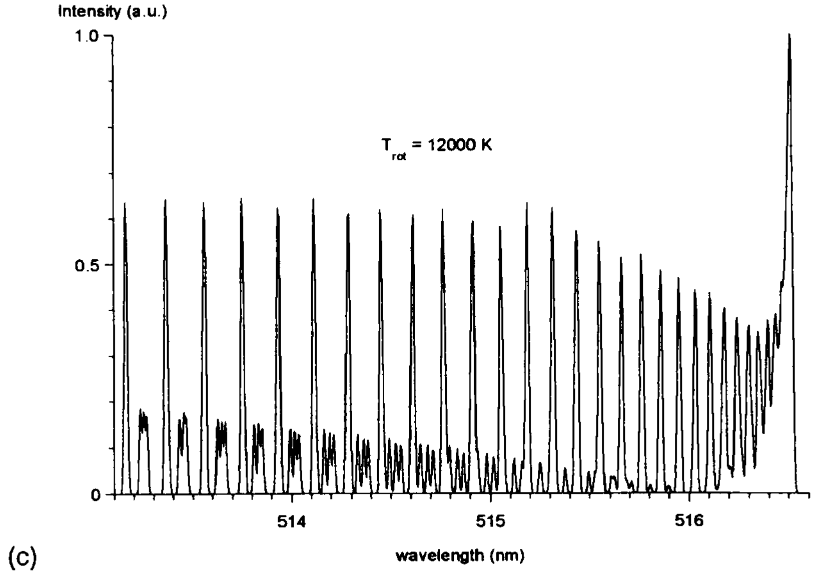

FIG. 1: Continued

First we calculate the maximum vibration number for each electronic state v_{max} by the comparison of the vibrational energy and the dissociation energy of the electronic state considered. Then Herzberg' s method of effective molecular potential [23,25] is used to calculate the maximum rotation number J_{max}. The electronic states $C_2(d^3\Pi_g)$ and $C_2(a^3\Pi_u)$ belong to Hund's intermediate coupling. The rotational term values for the triplets are written as [26] :

$$^3\Pi_2 \ : \ F_1(J) = B_v[J(J+1) - \sqrt{y_1 + 4J(J+1)} - \frac{2}{3}\frac{y_2 - 2\,J(J+1)}{y_1 + 4\,J(J+1)}] - D_v\,(J - \frac{1}{2})^4$$

$$^3\Pi_1 \ : \ F_2(J) = B_v[J(J+1) + \frac{4}{3}\frac{y_2 - 2\,J(J+1)}{y_1 + 4\,J(J+1)}] - D_v\,(J + \frac{1}{2})^4$$

$$^3\Pi_0 \ : \ F_3(J) = B_v[J(J+1) + \sqrt{y_1 + 4J(J+1)} - \frac{2}{3}\frac{y_2 - 2\,J(J+1)}{y_1 + 4\,J(J+1)}] - D_v\,(J + \frac{3}{2})^4$$

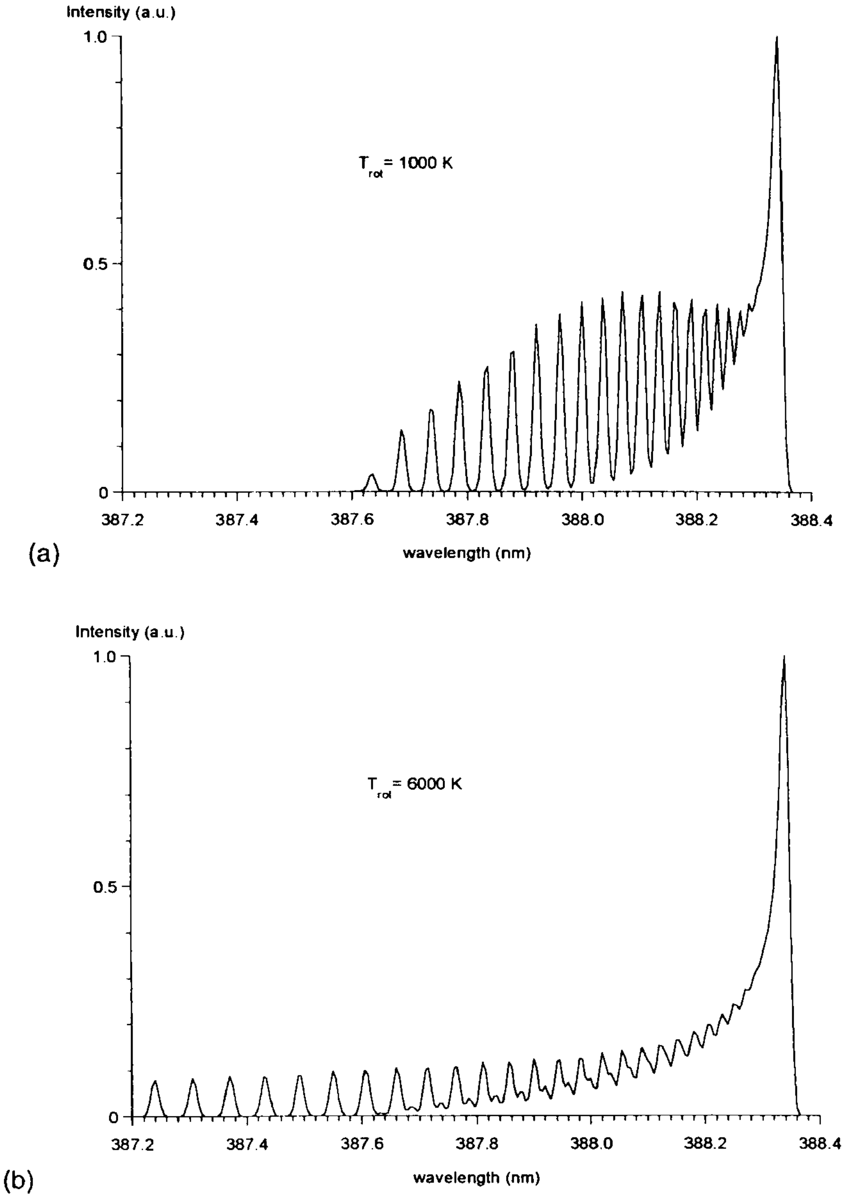

FIG. 2 : Simulated spectra : violet system of CN, (0-0) and (1-1) bands, FWHM = 0.014 nm. a) T_{rot} = 1000 K. b) T_{rot} = 6000 K. c) T_{rot} = 12000 K.

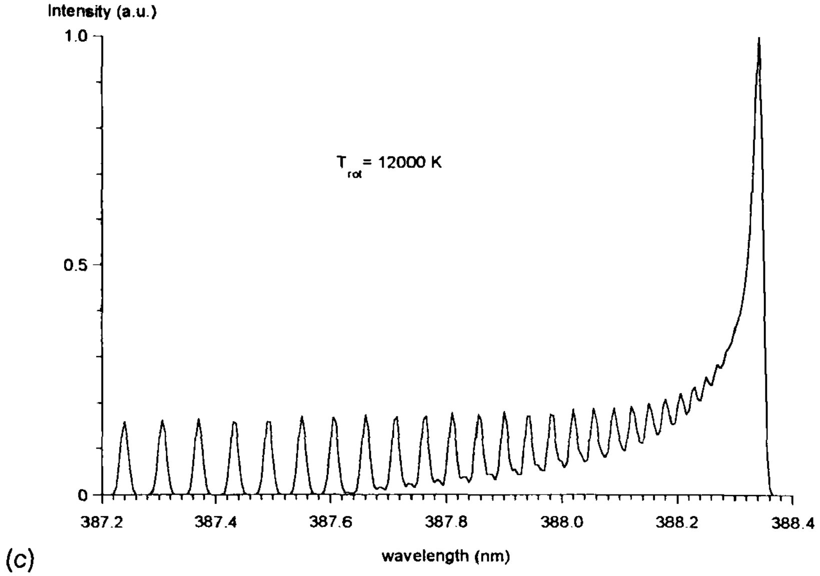

FIG. 2: Continued

with $y_1 = \Lambda^2\, Y(Y-4) + \frac{4}{3}$ and $y_2 = \Lambda^2\, Y(Y-1) - \frac{4}{9}$

and Y is the measure of the coupling force between the spin and the internuclear axis and Λ the orbital angular momentum.

The wavelengths of each rotational line are deduced. The calculated spectrum is then convoluted with the function of the apparatus. A Gaussian apparatus function of 0.014 nm full width at half maximum (FWHM) is determined experimentally with an atomic line of mercury. For each $I^{e'v'J'}_{e''v''J''}(\lambda)$, we apply the function :

$$I(\lambda) = I^{e'v'J'}_{e''v''J''} \exp\left(-\frac{(\lambda - \lambda^{e'v'J'}_{e''v''J''})^2}{2\sigma^2}\right)$$

where σ is the standard deviation and FWHM equal to $2.35 \times \sigma$.

The whole spectrum is the sum of the rotational lines of the ro-vibrational band. For the Swan system of C_2 and the violet system of CN, the Q-branches are not taken into account in the calculation because their intensities are negligible in comparison with R_i and P_i ($i = 1,2,3$) branches. The rotational spectrum involves high rotational levels. Some overlapping of P and R lines are observed. Figures 1a, 1b and 1c present the calculated spectra of C_2 for different temperatures. At low temperatures (1000 K) R branches are dominant but at high temperature ($T \geq 6000$ K) P branches are the most intense lines. Figures 2a, 2b and 2c present calculated spectra of CN for the same temperatures.

III EXPERIMENT

The experimental device is shown in Figure 3.

The wall stabilized arc is produced in a modified Maecker chamber which is described in details in Figure 4. This chamber is made of copper hallow cupels cooled with water. Bakelite cupels make it possible to electrically isolate copper cupels from one another and the tangential injection to the arc column of studied gas (CO_2-Ar mixture). Three mass flow controllers regulate the gas flows and adjust the ratio of different gases in the mixture. The copper anode and the tungsten cathode are protected with argon. The discharge current is adjusted with a DC generator from 10 A to 50 A. The light emitted is observed perpendicularly to the arc column. In order to obtain a good spatial resolution, we used a 25 cm focal lens. The wavelength selection is carried out by a 150 cm focal length monochromator (high resolution monochromator THR 1500 Jobin Yvon). An holographic grating with 2400 grooves per millimetre has been used. The resolution is 0.01 nm at 516 nm. Behind the monochromator the light is detected with an optical multichannel analyser (OMA 4000 EG&G). The CCD detector (matrix of 512 × 512 pixels) is a thermoelectrically cooled CCD based detector (-70°C). This detector is efficient for wavelengths ranging from 300 nm to 1.1 μm. Data are transferred to a PC computer to be analysed. Figures 5a and 5b present the experimental spectra of C_2 and CN.

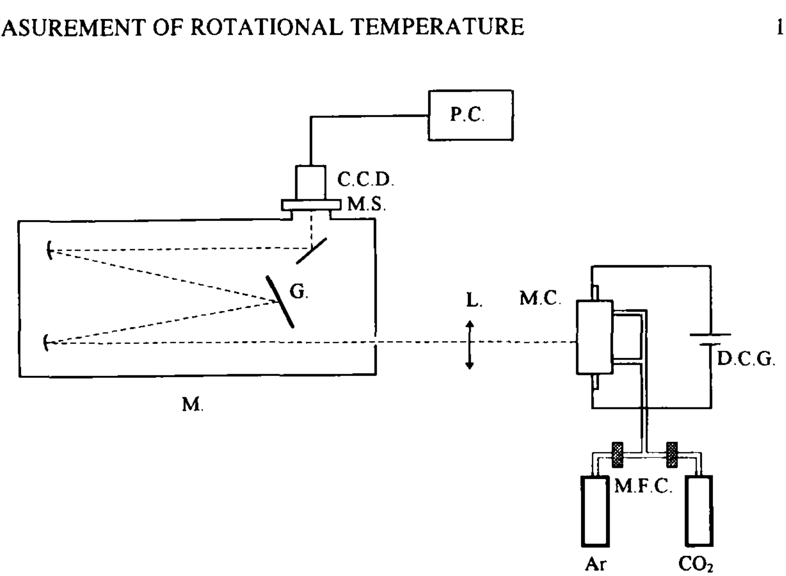

FIG. 3 : Experimental set up. M.C. : Maecker chamber, M.F.C. : mass flow controllers, D.C.G. : DC generator, L. : lens, M. : monochromator, G. : grating, M.S. : mecanic shutter, C.C.D. : CCD matrix, P.C. : microcomputer.

IV TEMPERATURE MEASUREMENT

The measurements are performed in an Ar-CO_2 mixture (5.5 % CO_2, 94.5 % Ar) at atmospheric pressure. The arc current is 25 A, the entrance slit of the monochromator 80 μm and the exposure time 1 s. The determination of the rotational temperature is obtained by the comparison of experimental spectrum with calculated spectra for different temperatures. We calculate :

$$\Theta = \sum_{i=1}^{N} \left(I_{exp}(i) - I_{sim}(i) \right)^2$$

where : I_{exp} (i) is the i-peak intensity of the experimental spectrum, I_{sim} (i) the i-peak intensity of the simulated spectrum for T_{rot} and N the total number of peaks. We have a Θ for each rotational temperature. So the rotational temperature

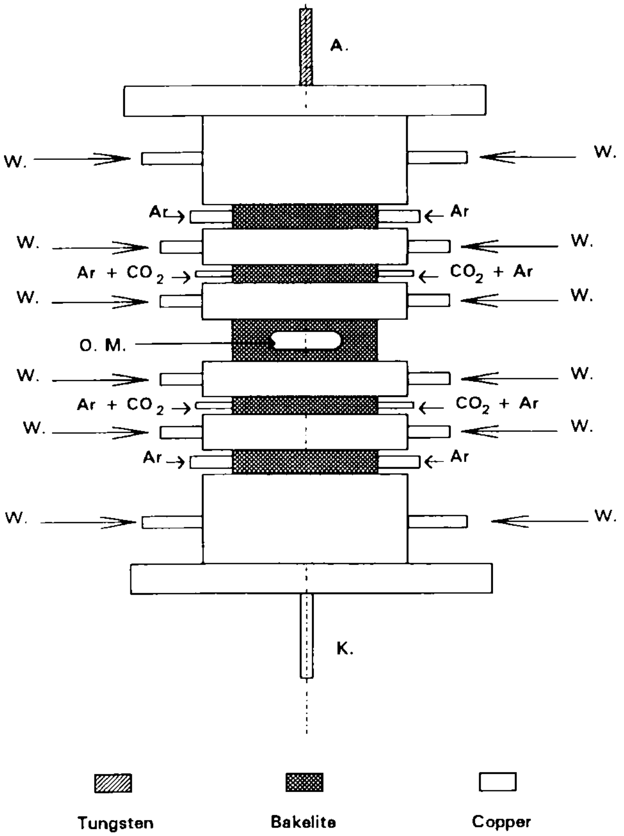

FIG. 4 : Modified Maecker chamber. K. : cathode, A. : anode, W. : water, O.M. : optical measurement.

corresponds to $\Theta(T_{rot})$ minimum. We must take into account the beginning of different branch disturbances. For the Swan system of C_2 and the violet system of CN, we only consider the peaks of the P_i branches to determine the temperature because in our temperature range they are the most intense lines. The number of peaks and the peaks chosen are shown in figures 5a and 5b - they are numbered. This choice can be explained by the very slight overlapping of these lines with other branches [27].

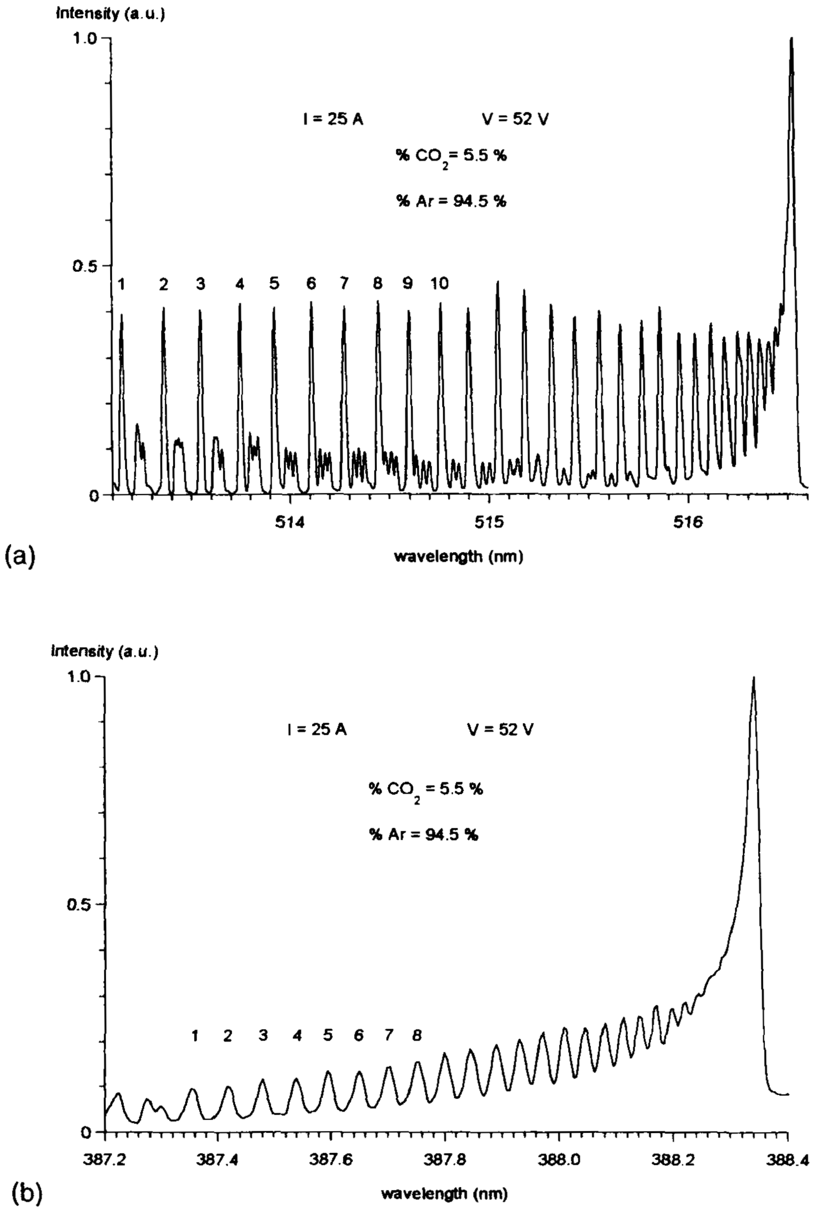

FIG. 5 : Experimental spectra : Ar-CO$_2$ mixture, 94.5 % Ar - 5.5 % CO$_2$, P = 1 atm, I = 25 A, Entrance Slit : 80 μm. a) Swan system of C$_2$, (0-0) band. b) Violet system of CN, (0-0) band

The rotational temperatures deduced are similar to C_2 and CN : 6500 K to the Swan system of C_2 and 5700 K to the violet system of CN.

The accuracy of this method depends first on the evolution of the calculated spectra in the studied wavelength range with the temperature, secondly on the intensity of the recorded signal. In our case the accuracy can be estimated at about 500 K.

V CONCLUSION

The optical emission spectroscopy technique gives a non perturbative and accurate temperature measurement. This method allows to determine the rotational temperature in molecular plasma. It can be used in any plasma where diatomic molecular species (molecules, radicals, ions) are present. The accuracy will depend on the evolution of the calculated spectra in the wavelength range studied with the temperature.

REFERENCES

1. P. ANDRE, Partition Functions and Concentrations in Plasmas Out of Thermal Equilibrium, IEEE Tranactions of Plasma Science, 1995 ; Vol. 23, n°3 : 453.

2. J. AUBRETON, C. BONNEFOI, J.M. MEXMAIN,Calculation of some Thermodynamic Properties and Transport Coefficients in a Thermal Nonequilibrium Ar-CO_2 Plasma at Atmospheric Temperature, Rev. Phys. Appl., 1986 ; Vol. 21, n°6 : 365.

3. V. LAGO, P. ASSELIN, P. LASGORCEIX, M. DUDECK, Mesure de la température et de la densité électronique par sondes électrostatiques modulées, 4^{ième} congrès de la division plasma de la SFP, Toulouse, 1994 ; B18.

4. D. WILDMAN, Quarterly Progress Report n°107. Research Laboratory of Electronics M.I.T., 73 (1972).

5. M. OSHIMA, Determination of Plasma Gas Temperature during Reactive Sputter Etching, Jpn. J. Appl. Phys. 1978 ; 17 : 1157.

6. S. DE BENEDICTIS, R. D'AGOSTINO, and F. CRAMASSORA, Spectroscopic Analysis of the Vibrational Distributions in Dissociative CO-He RF Discharges, Chem. Phys. 1982 ; 71 : 247.

7. G.P. DAVIS and R.A. GOTTSCHO, Measurement of Spatially Resolved Gas-Phase Plasma Temperatures by optical Emission and Laser Induced Fluorescence Spectroscopy, J. Appl. Phys. 1983 ; 54 : 3080.

8. N.V. CHEKALIN, V.S. LETOKHOV, V.N. LOKHMAN and A.N. SHIBANOV, Primary Products of Multiphoton Dissociation of the C_2H_4 Molecule in a Intense IR Field, Chem. Phys. 1979 ;36 : 415.

9. L. LESIECKI and W.A. GUILBORY, Low Pressure Infrared Multiple-Photon Photochemistry of Acetonitrile, J. Chem. Phys. 1978 ; 69 :, 4572.

10. H. REISLER, M. MANGIR and C. WITTIG, The Kinetics of Free Radicals Generated by IR Laser Photolysis. I. Reactions of $C_2(a^3\Pi_u)$ with NO, vinyl cyanide, and ethylene, J. Chem. Phys. 1979 ; 71 (5) : 2109.

11. S.E. BIALKOWSKI and W.A. GUILBORY, Collisionless Formation and Rovibronic Relaxation of CH and OH from the IR Multiphoton Photolysis of CH_3OH, J. Chem. Phys. 1978 ; 68 : 3339.

12. V.M. DONNELLY, D.L. FLAMM, C.W. TU, and D.E. IBBOTSON, Temperature Dependence of InP and GaAs Etching in a Chlorine Plasma, J. Electrochem. Soc. 1982 ; 129 : 2533.

13. B. BARBIERI, N. BEVERINI, and A.SASSO, Optogalvanic Spectroscopy Rev. Modern Phys. 1990 ; 62 : 603.

14. R. WALKUP, Ph. AVOURIS, R.W. DREYFUS, J.M. JASINSKI, and G.S. Selwyn, Mat. Res. Soc. Symp. Vol. 29. Elsevier Science Publishing Co., 1984.

15. J. BACRI and M. LAGRECA, Departures from CLTE Composition in a Nitrogen Arc at Atmospheric Pressure. I. experimental Results, J. Appl. D. : Appl. Phys., 1983 ; 16 : 829.

16. G. CERNOGORA, G. GOUSSET, L. HOCHARD, M. DUDECK, P. LASGORCEIX, V. LAGO, Rotational Temperature Measurements in an Arc Jet ; J.Thermophysics, 1991 Vol. 6, n°3 : 561.

17. G. CERNOGORA, G. GOUSSET, L. HOCHARD, M. DUDECK, P. LASGORCEIX, V. LAGO, , Rotational Temperature Measurements of N_2^+ in an Arc Jet at Low Pressure, AIAA 92-2967 23rd Plasmadynamics and Laser Conference, 1992.

18. G.M. GRIGORIAN, Yu. Z. INIKH and N.V. CHERNYSHEVA, Intensity Distribution in the Rotational Structure of Swann Bands of the C_2 Molecule in a Discharge Afterglow in a He-CO Mixture, Opt. Spectrosc. 1991 ; 70 (2) : 180.

19. J.W. RICH and R.C. BERGMAN, C_2 and CN Formation by Optical Pumping of CO/Ar and CO/N_2/Ar Mixtures at Room Temperature, Chem. Phys. 1979 ; 44 : 53.

20. C. KUNZ, P. HARTECK, S. DONDES, Mechanism for Excitation of the C_2 High-Pressure Bands, J. Chem. Phys. 1967 ; 46 : 4157.

21. T.J. COOK and D.H. LEVY, Lifetimes of the $A^2\Pi$ and $B^2\Sigma$ States of the CN Radical, J. Chem. Phys. 1972 ; 57 : 5059.

22. C.K. LUK and R. BERSOHN, Time Dependence of the Fluorescence of the B state of CN, J. Chem. Phys. 1973 ; 58 : 2153.

23. G. HERZBERG, Molecular spectra and molecular structure. Vol. I, Spectra of Diatomic Molecules. Van Nostrand Compagny; INC. 1950.

24. KOVACS, Rotational structure in the spectra of diatomic molecules. Adam Hilger LTD - London 1969.

25. K.S. DRELLISHAK, D.P. AESCHLIMAN, and A. B. CAMBEL, Partition Functions and Thermodynamic Properties of Nitrogen and Oxygen Plasmas, The Physics of Fluids, 1965 ; Vol. 8, n°9 : 1590.

26. A. BUDO, Rotation Constants of TiO, C_2, PH, AlH and NH, Zs. F. Phys. 1936 ; 98 : 437.

27. A. CZERNIKOSWSKI, Ch. de IZARRA and H. LESUEUR, Rotational Temperatures Evaluation in a CO_2 + N_2 Arc From Partially Resolved CN and C_2 Molecular Band.;ISPC-8 Tokio. 1987; P-033.

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