

TEMPERATURE MEASUREMENT BASED ON C₂ SWAN SPECTRUM
IN A TRANSFERRED ARC IN CH₄ + CO₂ MIXTURE

H. Nassar*, K. Meguernes**, A. Czernichowski,
and J. Chapelle

Université d'Orléans, Faculté des Sciences,
45067 Orléans cedex 2, France

The C₂ d³Π_g - a³Π_u band emitted from a 5 kW arc fed by CH₄/CO₂/Ar mixture are recorded with the help of an optical system consisting of a linear CCD array coupled with a 2-m spectrometer. The rotational temperature of 4800 ± 300 K is found from the experimental, Abel inverted spectrum in the arc center after a point-to-point comparison of the spectrum with a computer simulated one.

1. Introduction

Great attention is being paid at the present time to the transformation of carbon dioxide and methane, the cheapest carbon-containing feed stock, into more valuable compounds. Energy efficient reforming of CH₄ with CO₂ would be therefore a particularly interesting process for producing synthesis gas from two green house gases :



The product can be then used for the catalytic synthesis of hydrocarbon fuels or valuable oxygenated chemicals.

Both thermal or non-equilibrium plasmas have been proposed to perform this endothermal reaction without catalysts. Some results from our Orleans' group described in [1-6] concern laboratory scale investigation of the reaction in plasma reactors based on transferred-arcs or on so-called gliding discharges (GlidArc).

present addresses :

* Université Libanaise, Faculté des Sciences,
Zahlé-Bekaa, Lebanon

** Université de Tizi-Ouzou, Département de Physique,
15000 Tizi-Ouzou, Algeria

Several optical methods have been used in our group since early seventies in order to determine plasma parameters. One of these methods is based upon an analysis of partially resolved emission spectrum of CN [7,8], C₂ [8,9], N₂⁺ [10-13], OH [14,15], CH [16] or N₂ [17] molecule in the UV or visible range. The spectra give a quite easy access to the vibrational and/or rotational plasma temperatures (if any). The method is therefore used in order to answer some questions on thermodynamic equilibria in a plasma produced from the reactive CH₄ + CO₂ mixture in a transferred-arc reactor.

2. Experimental set-up

2.1. Reactor

The reactor consists of an arc chamber to which an Argon plasma jet of 4 mm diameter emerges through a 2 kW plasma torch nozzle considered as a first anode. This jet makes a first ionization stage. Another tubular transfer anode (5 mm of internal dia.) put at 20 mm from the nozzle aperture allows to obtain a DC transferred arc in which methane and carbon dioxide gases are introduced (see Fig. 1). Both copper anodes as well as the torch tungsten cathode are water cooled. The transferred arc chamber is fed at atmospheric pressure by CH₄/CO₂ = 1 (molar ratio) gas mixture at 10 slm flow rate. The electrical power supplied to the arc is 5 kW.

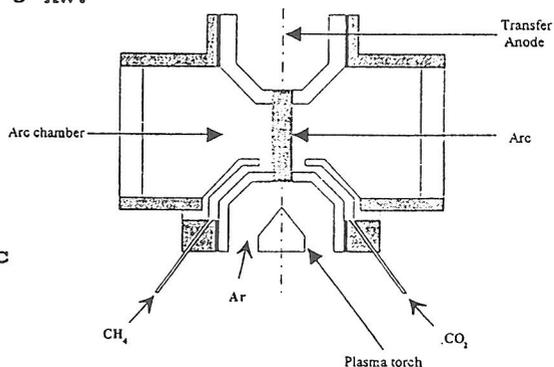


Fig. 1. Transferred-arc reactor

2.2. Spectral recording system

The C₂ emission spectra are observed with the help of a 2-meter monochromator equipped with a 1200 groves/mm grating coupled with an optical analyzer based on Thomson linear CCD array (1728 pixels of 13.39 m). The transferred arc column at the half of its lengths is scanned through a quartz window by a step-motor desk computer moved optical system at 12 points at 0.45 mm step.

3. Temperature measurement

3.1. Simulation of the $d^3\Pi_g-a^3\Pi_u$ spectrum of C_2

The absolute rotational emission line intensity of the molecule is given by Herzberg [18] :

$$I = C \cdot \nu^4 \cdot S_{J'J''} \cdot \exp\left[-\frac{hc \cdot F(J')}{kT}\right] \quad (1)$$

where C is a normalization constant, ν is the wave number, $S_{J'J''}$ is the Hönl-London factor, $F(J')$ is the spectral terms and T is the temperature (marks ' concern the lower spectral term and marks '' are for the upper ones). Formulae for $S_{J'J''}$ factors for the intermediate a-b Hund's case are taken from Kovacs [19] and the spectral terms are those of Budo [20].

Computed spectrum of individual lines for a given temperature is then convoluted with our apparatus function approximated by the Gauss function whose $DX = 0.3 \text{ cm}^{-1}$ (the half-width at $1/e$ height) :

$$I_0 = \int_{\nu_0 - \varepsilon}^{\nu_0 + \varepsilon} I \cdot \exp[-(\nu - \nu_0)/DX]^2 d\nu \quad (2)$$

where $\varepsilon = 2.5 \cdot DX$ and ν_0 is the wavenumber of the line.

An integrated cell (pixel) of simulated spectrum is chosen according to the cell of experimental spectrum under consideration. We can, following the situation, group several cells in one.

3.2. Numerical method for rotational temperature evaluation

To evaluate the temperature from a given real spectrum, we have chosen to compare point-by-point this spectrum with spectra simulated at different temperatures. Our best-fit criterion is based on a minimization of the quantity $E(T)$ defined as :

$$E(T) = \frac{1}{N} \cdot \left[\sum_{i=1}^N (I_i^r - I_i^s)^2 \right]^{1/2} \quad (3)$$

I_i^r et I_i^s are respectively the intensities of the real and simulated i -th pixel of the spectrum containing N points. If the choice of the spectrum reference origin (background) is a bad one, the result will be affected. To avoid this error, we fix several origins, and our computer program searches the best origin to find the $E(T)$ at minimum.

3.3. Results

Twelve spectra records (665 wavelengths points each) were Abel inverted in order to present a local intensity distribution as a function of the radial distance from arc column center. Such distributions are then compared to spectra simulated at large temperature ranges. An example of real (experimental) spectrum and corresponding simulated one is shown on Fig. 2. The resulting rotational temperature profile in the transferred arc column is shown on Fig. 3.

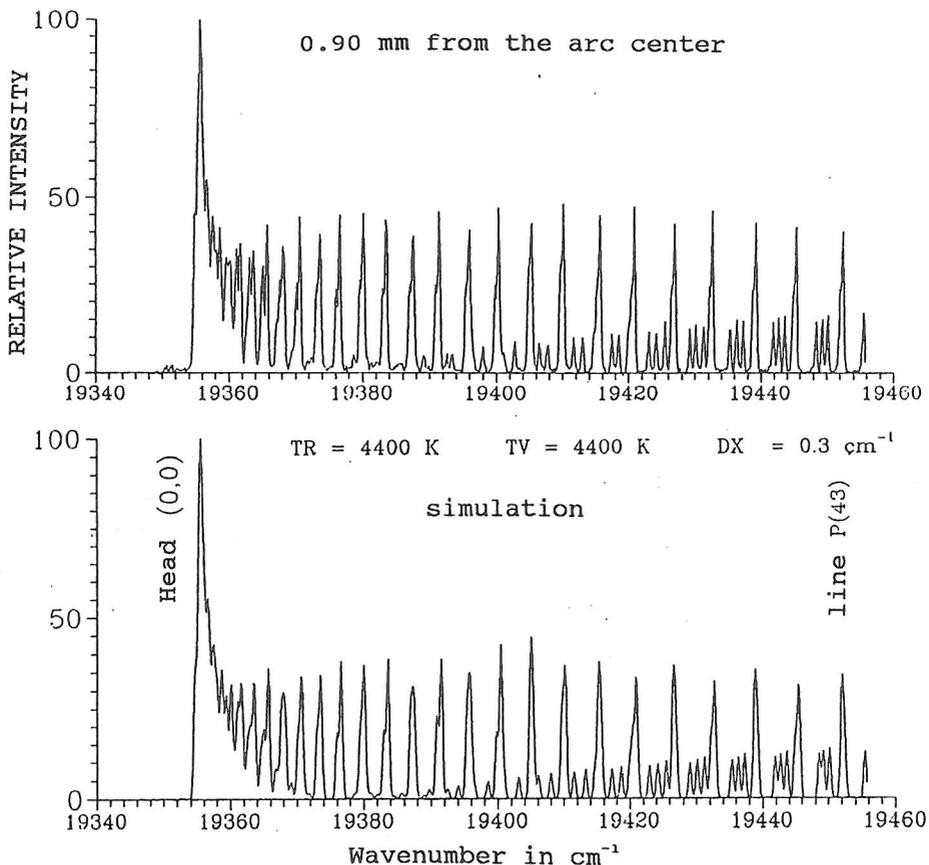


Fig. 2. Example of an experimental spectrum at 0.90 mm from the arc column center (after the Abel inversion), and corresponding simulated spectrum.

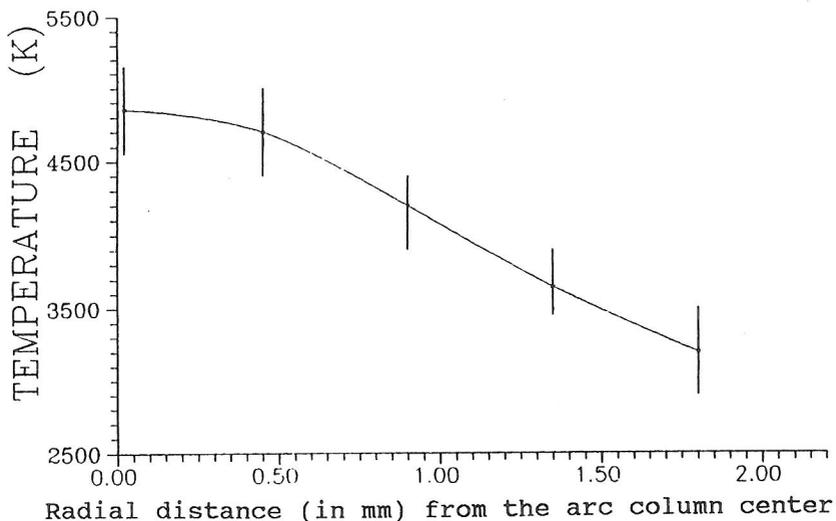


Fig. 3. Radial distribution of the rotational temperature in our transferred electric arc column in Ar/CO₂/CH₄ mixture.

4. Discussion and conclusion

The rotational temperature of about 4800 ± 300 K has been found from the experimental spectrum in the arc column center while at the column fringes the temperature drops to 3200 ± 300 K at 1.8 mm from the axis. This last point was obtained from a quite weak and noisy spectrum.

A calculation based on Limoge's computer program [21] of the complete thermodynamic equilibrium for the same CH₄/CO₂/Ar gas mixture (H/C/O/Ar = 1/0.485/0.463/0.168 in moles) shows that the C₂ molecule concentration in plasma reaches its maximum at about 4200 K and then drops by two orders of magnitude at about 3200 K. The temperatures for which this molecule can be used as a "thermometer" cover therefore a region from about 3500 to 5000 K.

Another thermodynamic analysis based on [21] shows however that one needs to heat up the same gas mixture to only 1200 K in order to obtain the total transformation of the mixture to the synthesis gas. The thermal plasma of the transferred arc seems therefore be too hot (and therefore too expensive) for an industrial application. Much better results can be obtained when using a non-thermal powerful electrical discharges like GlidArc [5].

References

1. P. Jörgensen, J. Chapelle, A. Czernichowski, K. Meguernes, ISPC-8, Tokyo, 1987, 2, 695.
2. K. Meguernes, J. Chapelle, A. Czernichowski, ISPC-9, Pugnochiuso (Italy), 1989, 693.
3. H. Lesueur, A. Czernichowski, J. Chapelle, J. de Phys., 51, C5-49 (1990).
4. K. Meguernes, J. Chapelle, A. Czernichowski, J. High Temp. Chem. Process., 1, 71 (1992).
5. K. Meguernes, J. Chapelle, A. Czernichowski, ISPC-11, Loughborough (England), 1993, 2, 710.
6. H. Lesueur, A. Czernichowski, J. Chapelle, Int. J. Hydrogen Energy, 19, 139 (1994).
7. A. Czernichowski, J. Chapelle, "Ampère, 150 Ans Après", Conf. Proc., Paris, 1986, 157.
8. A. Czernichowski, Ch. de Izarra, H. Lesueur, ISPC-8, Tokyo, 1987, 1, 443.
9. A. Czernichowski, ISPC-8, Tokyo, 1987, 1, 437.
10. A. Czernichowski, J. Phys. D, 20, 559 (1987).
11. H. Nassar, A. Czernichowski, J. de Phys., 51, C5-289 (1990).
12. H. Nassar, A. Czernichowski, ISPC-11, Loughborough (England), 1993, 1, 487.
13. H. Nassar, A. Czernichowski, Acta Physica Polonica A, 84, 215 (1993).
14. A. Czernichowski, Soc. Franç. des Thermiciens, Châtenay-Malabry, France, 1987, Conf. Proc., Com. 42.
15. M. Beaulieu, A. Czernichowski, D. Gravelle, M.I. Boulos, T. Sakuta, ISPC-8, Tokyo, 1987, 1, 377.
16. J. Kouliadiati, A. Czernichowski, J.J. Beulens, D.C. Schram, J. de Phys. 51, C5-297 (1990).
17. E. Pawelec, M. Simek, H. Nassar, A. Czernichowski, K. Musiol, L. Dittrichova, sent to Acta Physica Polonica A.
18. G. Herzberg, Spectra of Diatomic Molecules, vol. 1 of "Molecular Spectra and Molecular Structure", 1950.
19. I. Kovacs, Rotational Structure in the Spectra of Diatomic Molecules, Adam Hilger, London, 1969.
20. A. Budo, Z. Phys., 105, 582 (1963).
21. G. Delluc, M.F. Elchinger, B. Pateyron, ADEP Software, Université de Limoges, France.