

# Absorption spectroscopy measurements of atomic and molecular carbon population densities in an expanding thermal arc plasma

**Citation for published version (APA):**

Otorbaev, D. K., Buuron, A. J. M., Gielen, J. W. A. M., Sanden, van de, M. C. M., & Schram, D. C. (1995). Absorption spectroscopy measurements of atomic and molecular carbon population densities in an expanding thermal arc plasma. *Diamond and Related Materials*, 4(7), 108-911. [https://doi.org/10.1016/0925-9635\(94\)00248-7](https://doi.org/10.1016/0925-9635(94)00248-7)

**DOI:**

[10.1016/0925-9635\(94\)00248-7](https://doi.org/10.1016/0925-9635(94)00248-7)

**Document status and date:**

Published: 01/01/1995

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

# Absorption spectroscopy measurements of atomic and molecular carbon population densities in an expanding thermal arc plasma\*

D.K. Otorbaev, A.J.M. Buuron, J.W.A.M. Gielen, M.C.M. van de Sanden, D.C. Schram

*Department of Physics, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, Netherlands*

Received 30 September 1994

## Abstract

Absolute population densities of argon and atomic and molecular carbon are determined using the method of reabsorption in an expanding thermal arc plasma during the deposition of amorphous hydrogenated carbon (a-C:H) coatings. The reactor conditions were the following: background pressure 20–200 Pa, argon flow rate 58–116 cm<sup>3</sup> s<sup>-1</sup>, arc current 45 A, arc voltage 70–80 V; hydrocarbons (CH<sub>4</sub> or C<sub>2</sub>H<sub>2</sub>) with a flow rate of 3–6 cm<sup>3</sup> s<sup>-1</sup>, were injected either into the nozzle of the arc or directly into the vessel. Depending on the argon–methane/acetylene gas mixture and the hydrocarbon injection (downstream or in the nozzle), the stationary positive or negative absorption between the quantum states of Ar(3p<sup>5</sup>4p → 3p<sup>5</sup>4s) ( $\lambda = 696.5$  nm), C(2p<sup>2</sup>3s → 2p<sup>2</sup>1s) ( $\lambda = 247.9$  nm) and C<sub>2</sub>(d<sup>3</sup>Π<sub>g</sub>, v' = 0 → a<sup>3</sup>Π<sub>u</sub>, v'' = 0) (band head at  $\lambda = 516.5$  nm) is determined. From this absorption the absolute population densities of the radicals in the plasma are obtained. Depending on the plasma conditions, the density of the argon first excited state Ar(3p<sup>5</sup>4s, <sup>3</sup>P<sub>2</sub>) was about 10<sup>16</sup>–10<sup>17</sup> m<sup>-3</sup>, whereas the atomic and molecular carbon densities were of the order of 10<sup>18</sup>–10<sup>19</sup> m<sup>-3</sup>.

**Keywords:** Spectroscopy; Plasma jet CVD; Cold plasma; Plasma diagnostics

## 1. Introduction

In a recombining plasma, favourable conditions for population inversion between quantum states can occur. The atomic and molecular excited states are populated by the recombining flux going from the ionized states to the ground electronic states of the neutrals. The phenomenon known as amplification in a recombining plasma has been predicted theoretically [1] and demonstrated experimentally for the transitions between the excited states of various atoms [2,3]. In this paper absorption spectroscopy has been applied to measure the absolute densities of atomic and molecular carbon during the deposition of amorphous hydrogenated carbon (a-C:H) coatings by an expanding thermal arc plasma. A stationary population inversion between the electronic quantum states of the C<sub>2</sub> molecule is observed for the first time.

## 2. Experimental methods

The experiments are carried out in the expanding thermal plasma produced by a cascaded arc, described

in detail elsewhere [4,5]. In the cascaded arc a thermal plasma in argon is created in a cylindrical channel (diameter 4 mm) with a temperature of about 1 eV at a subatmospheric pressure of about 5 × 10<sup>4</sup> Pa. This plasma expands into a low pressure vessel through a conically shaped nozzle. Hydrocarbons (CH<sub>4</sub> or C<sub>2</sub>H<sub>2</sub>) are injected either at the end of the arc channel (nozzle) or into the vessel in the early expansion. By means of excitation and charge exchange a beam of ionized and excited particles (Ar<sup>\*+</sup>, (C<sub>x</sub>H<sub>y</sub>)<sup>\*+</sup>, C<sub>n</sub><sup>\*+</sup>, H<sub>n</sub><sup>\*+</sup>) is created. The particles from the arc are accelerated to supersonic velocities of up to 4000 m s<sup>-1</sup>, pass through a shock and are transported further at subsonic velocities. For typical pressures in the vessel of about 10<sup>2</sup> Pa the shock is observed at about 40 mm from the nozzle [4–6]. The plasma conditions under which the experiments have been performed are the following: background pressure 20–200 Pa, argon flow rate 58–116 cm<sup>3</sup> s<sup>-1</sup>, hydrocarbon flow rate 3–6 cm<sup>3</sup> s<sup>-1</sup>, arc current 45 A, arc voltage 70–80 V.

The spectral line intensity measurements are performed by the optical system presented in Fig. 1, which consists of one concave mirror and a system of plane mirrors and lenses. The measurements are made 20 and 70 mm downstream of the arc nozzle, perpendicularly

\* Paper presented at Diamond Films '94, Il Ciocco, 25–30 September 1994.

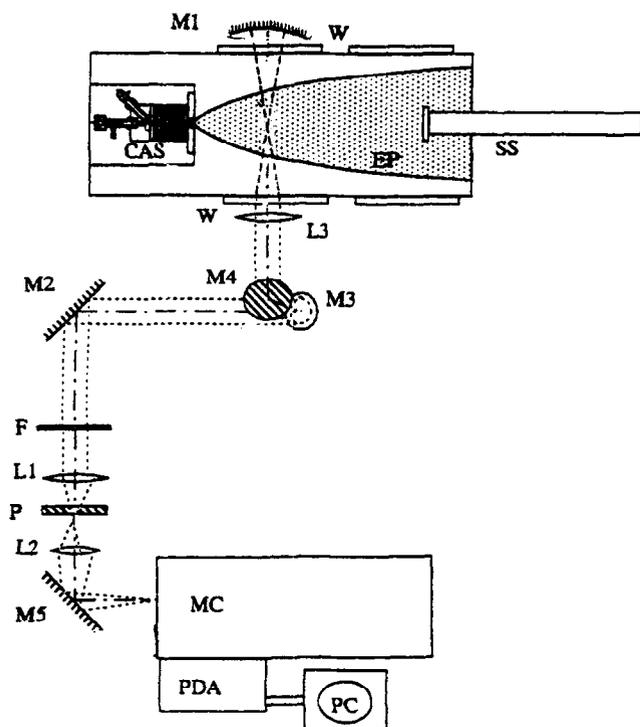


Fig. 1. An expanding cascaded arc plasma and absorption spectroscopy set-up: CAS, plasma source (cascaded arc); EP, expanding plasma; SS, substrate support; W, window; F, order filter; L1–L3, lenses; M1–M5, mirrors; P, diaphragm; MC, monochromator; PDA, photodiode array; PC, personal computer.

to the axis of the expanding plasmas. The optical signal detection section consists of a high resolution monochromator with a focal length of 1 m and a grating with  $1200 \text{ lines mm}^{-1}$ , together with a Peltier-cooled photodiode array. With this set-up a spectral range of about 20 nm with a resolution of 0.02 nm can be covered simultaneously. The system was calibrated by positioning a tungsten ribbon lamp in the vessel and recording the spectrum at a known true temperature of the ribbon.

The positive or negative absorption between the quantum states can be observed by measuring the apparent absorption coefficient of the spectral lines. Quantitatively an integral absorption coefficient has to be determined,  $\int_0^\infty k_\nu d\nu$ , which for a homogeneous medium is given by [7]

$$\int_0^\infty k_\nu d\nu = \frac{\lambda_0^2}{8\pi} \frac{g_k}{g_i} A_{ki} n_i \left( 1 - \frac{g_i n_k}{g_k n_i} \right) \quad (1)$$

where  $k_\nu$  is the absorption coefficient,  $n_i$  and  $n_k$  are the total population densities of the particles on lower and upper quantum levels respectively,  $g_i$  and  $g_k$  are their respective statistical weights,  $A_{ki}$  is the transition probability (Einstein coefficient) for spontaneous emission and  $\lambda_0$  is the central line wavelength.

To measure the absorption coefficient  $k_\nu$ , the method of reabsorption with a mirror [7] has been used. In that case a concave mirror ( $f = 25 \text{ cm}$ ) of reflectance  $r$  was

placed behind the plasma (see Fig. 1) and the line intensity was measured with the mirror covered ( $I_1$ ), or not covered ( $I_2$ ). The line absorption function  $A_L$ , defined as the ratio of the absorbed to the incident radiation, was measured:

$$A_L = \frac{\Delta I}{rI_1} = \frac{I_1 + rI_1 - I_2}{rI_1} \quad (2)$$

where  $\Delta I$  is the absorbed radiation and  $I_1$  and  $I_2$  are the radiations from the plasma with the mirror covered and open respectively.

The relation between  $A_L$  and  $k_\nu$  is given by [7]

$$A_L = 2 - \frac{\int_0^\infty [1 - \exp(-2k_\nu l)] d\nu}{\int_0^\infty [1 - \exp(-k_\nu l)] d\nu} \quad (3)$$

where  $l$  is the absorption length.  $A_L$  as function of  $k_\nu$  is tabulated, for example, in Ref. [7].

The mirror reflectance coefficient  $r(\lambda)$  is measured using a spectral line for which the plasma is optically thin. In that case  $\Delta I = 0$  in Eq. (2) and for known  $I_1$  and  $I_2$  values one can determine  $r(\lambda)$ . The measured  $r(\lambda)$  is the effective reflectance coefficient, which includes the transmittance coefficient of the vessel windows.

### 3. Results and discussion

To investigate the validity of the method, it was first applied to measure the density of argon in the first excited state  $\text{Ar}(3p^5 4s)$ . The experiments were performed in a pure argon plasma at an axial position of  $x = 70 \text{ mm}$  from the nozzle of the arc. The pressure in the vessel was 40 Pa and the gas flow rate  $58 \text{ cm}^3 \text{ s}^{-1}$ . For this condition the  $\text{Ar}(3p^5 4s)$  density was recently measured accurately using an external bright light source [5]. Self-absorption of the spectral line  $\lambda = 696.5 \text{ nm}$  (radiative transition  $\text{Ar}(3p^5 4p \rightarrow 3p^5 4s)$ ) is used to determine the absolute density of the  $\text{Ar}(3p^5 4s, ^3P_2)$  state. Another spectral line of argon,  $\lambda = 693.8 \text{ nm}$ , belongs to the same spectral range. However, that line is the result of another radiative transition  $\text{Ar}(3p^5 4d \rightarrow 3p^5 4p)$ . From the absolute emission intensity of the spectral line  $\lambda = 696.5 \text{ nm}$  the absolute density of the  $\text{Ar}(3p^5 4p)$  state has been determined. The measured density  $n_{\text{Ar}(4p)} \approx 5 \times 10^{13} \text{ m}^{-3}$  was in a good agreement with the previously reported result [4]. Calculations based both on the information about radiative transition probabilities and on the experimental data show that the analysed expanding plasma is transparent for the argon spectral line  $\lambda = 693.8 \text{ nm}$ . Therefore the radiation of this line is used to measure the reflectance coefficient of the mirror. A value of  $r = 0.65 \pm 0.03$  at  $\lambda = 693.8 \text{ nm}$  was found.

Table 1

Experimental conditions and measured values of absorption function  $A_L$  for the argon line  $\lambda = 696.5$  nm ( $3p^54p \rightarrow 3p^54s$  transition) and for the band head of the Swan system of  $C_2$  ( $d^3\Pi_g, v' = 0 \rightarrow a^3\Pi_u, v'' = 0$  transition)

Gas mixture	Flow rate ( $\text{cm}^3 \text{ s}^{-1}$ )	$C_xH_y$ injection	Axial position (nm)	Pressure (Pa)	$A_L$
Ar	58	—	70	40	0.29
CH <sub>4</sub> /Ar (1:20)	61	Nozzle	70	50	-0.25
CH <sub>4</sub> /Ar (1:20)	61	Nozzle	70	100	-0.36
CH <sub>4</sub> /Ar (1:20)	61	Nozzle	70	200	-0.30
CH <sub>4</sub> /Ar (1:40)	119	Nozzle	70	100	-0.17
CH <sub>4</sub> /Ar (1:10)	64	Nozzle	70	100	-0.55
CH <sub>4</sub> /Ar (1:20)	61	Vessel	70	100	-0.06
C <sub>2</sub> H <sub>2</sub> /Ar (1:20)	61	Nozzle	70	100	0.16
C <sub>2</sub> H <sub>2</sub> /Ar (1:20)	61	Vessel	70	100	0.10
CH <sub>4</sub> /Ar (1:20)	61	Nozzle	20	100	0

The experimental value of the line absorption function  $A_L$  for  $\lambda = 696.5$  nm in pure argon plasma is given in Table 1.

As measured using Thomson–Rayleigh scattering, the parameters for this plasma setting are the following:  $n_e \approx 3 \times 10^{19} \text{ m}^{-3}$ ,  $T_e \approx 3000$  K,  $n_0 \approx 5 \times 10^{20} \text{ m}^{-3}$  [4,6]. The estimated Voigt parameter  $a \ll 1$ , so that the Doppler limit (with the heavy particle temperature  $T_0 \approx 3000$  K [4,5]) for the Voigt function applies. The value for the absorption length has been derived from the lateral profile of the transparent line  $\lambda = 693.8$  nm emissivity. For typical experimental conditions it was found that  $l = 35$  mm (see also [5]).

Using Eqs. (1) and (3) and measured  $A_L$  values for the line  $\lambda = 696.5$  nm, the average absolute density of the  $\text{Ar}(3p^54s, ^3P_2)$  state is  $n_{\text{Ar}(4s)} \approx 2 \times 10^{17} \text{ m}^{-3}$ . This value is in good agreement with detailed measurements of Buuron et al. [5]. It clearly indicates that the method using the concave mirror is a simple but effective experimental procedure. The disadvantage is that it is not possible to measure the local particle densities in a non-homogeneous plasma with the current set-up. The experimental accuracy of the procedure is limited by the errors during the determination of  $r$  and  $A_L$ . We estimate the error in the density determination by the discussed method to be within a factor of 2.

The Swan system of  $C_2$  ( $d^3\Pi_g, v' = 0 \rightarrow a^3\Pi_u, v'' = 0$  transition, band head at  $\lambda = 516.5$  nm) has been used to measure the  $C_2$  molecular density in the plasma. Two spectral lines of argon,  $\lambda_1 = 516.2$  nm (transition  $\text{Ar}(3p^56d \rightarrow 3p^54p)$ ) and  $\lambda_2 = 518.8$  nm (transition  $\text{Ar}(3p^55d \rightarrow 3p^54p)$ ), belong to the same spectral range. The lower state of the radiative transition for these lines is the same as for the line  $\lambda = 693.8$  nm, but their transition probabilities are smaller than for the line  $\lambda = 693.8$  nm [8]. This means that for the plasma under investigation these transitions are optically transparent

as well and their emissivity could be used to measure the reflectance coefficient of the mirror. The measurements for the particular wavelength range gave a value of  $r = 0.74 \pm 0.04$ .

The values of the line absorption function  $A_L$  obtained for the band head of the Swan system of  $C_2$  ( $d^3\Pi_g, v' = 0 \rightarrow a^3\Pi_u, v'' = 0$  transition) under various experimental conditions in both argon/acetylene plasmas are given in Table 1. As can be seen, at the axial position  $x = 70$  mm, i.e. in the subsonic part of the expansion, for all conditions with methane injection into the reactor a negative absorption takes place ( $A_L$  is negative). For larger methane admixtures and for methane injection into the nozzle the effect is more pronounced. At the same time the absorption is absent at the position  $x = 20$  mm and is positive at  $x = 70$  mm when acetylene is injected into the reactor. Since the Voigt parameter for the rovibronic spectral lines of the Swan system was rather small,  $a \ll 1$ , again the Doppler limit (with the temperature  $T \approx 3000$  K [4,5]) for the Voigt function applies. The Einstein coefficients, Franck–Condon factors and Hönl–London factors for the Swan bands, needed for the calculation of  $C_2$  densities from the spectral line intensities, were taken from Ref. [9]. The values of the absorption length under various plasma conditions were derived by lateral scanning of the spectral line emissivities.

The negative values of the line absorption function  $A_L$  give fairly large population inversions. The total density of excited  $C_2(d^3\Pi_g, v' = 0)$  molecules for the experimental conditions presented in Table 1, gives  $n_{C_2(d^3\Pi)}$  in the range from  $2 \times 10^{18}$  to  $1.5 \times 10^{19} \text{ m}^{-3}$ . Overlapped molecular spectral line absorption has been treated as in Ref. [7] (see also Ref. [10]). For the conditions with a negative absorption only the density of the upper state of the transition can be determined. At the same time, when acetylene is injected into the reactor, the absorption is positive, and the absolute density of  $C_2$  molecules in the lower state  $C_2(a^3\Pi_u, v'' = 0)$  can be derived. For the conditions presented in Table 1  $n_{C_2(a^3\Pi)}$  was in the range  $(3-5) \times 10^{18} \text{ m}^{-3}$ . Note, however, that the measured  $A_L$  values as well as the molecular densities are averaged across the plasma beam, so the local absolute values of the absorption function and of the densities may be even larger.

As is seen from Table 1, in the supersonic part of the expansion (axial position  $x = 20$  mm)  $A_L$  is very close to zero. This means that either the densities of states are small enough, i.e. the absorption signal is below the detection limit, or the densities of upper and lower states are large but equal to (or comparable with) each other (see Eq. (1)). A major difference between the injections of methane and acetylene into the reactor is the sign of  $A_L$  (see Table 1). As an explanation it seems reasonable to assume that with acetylene injection into the reactor the direct collisional and/or thermal dissociation reac-

tion  $C_2H_2 \rightarrow C_2 + H_2$  becomes most important. Probably this reaction mainly populates the low-lying electronic states of  $C_2$ , which leads to a positive absorption.

The method has also been applied to atomic carbon absolute density determination using the spectral line  $\lambda = 247.9$  nm (radiative transition  $C(2p3s, ^1P_1 \rightarrow 2p^2, ^1S_0)$ ). In this spectral range we unfortunately did not find any other spectral lines or continuum emission to which the plasma under consideration was optically thin. In order to measure the reflectance coefficient of the mirror in that case, the emission of the same carbon line was used, but in two specific experimental regimes where the plasma is thought to be optically transparent to radiation with  $\lambda = 247.9$  nm. In the first regime the measurements were performed in the supersonic expansion, where, as mentioned, no absorption of  $C_2$  has been observed. In the second regime the total gas pressure in the vessel was decreased to 20 Pa. Both experimental regimes lead to the same value of  $r = 0.50 \pm 0.05$  at  $\lambda = 247.9$  nm.

For the injection of methane ( $CH_4/Ar = 1:20$ ) into the nozzle of the arc with a total gas flow rate of  $61 \text{ cm}^3 \text{ s}^{-1}$ , the  $A_L$  values for atomic carbon in the subsonic part of the expansion were always negative, ranging from  $A_L = -0.16$  (at  $p = 50$  Pa) to  $A_L = -0.88$  (at  $p = 200$  Pa). Applying the same calculation procedure as for  $C_2$ , the atomic carbon absolute density in the excited state  $C(2p3s, ^1P_1)$  can be estimated. The densities averaged across the plasma beam were in the range  $n_C = (2-9) \times 10^{18} \text{ m}^{-3}$ . These  $C(2p3s, ^1P_1)$  atomic densities are of the same order of magnitude as measured in the free-jet stream produced in a constricted arc [2].

#### 4. Conclusions

To understand the physical mechanism of the population inversion between the electronic quantum states of C and  $C_2$  radicals in an expanding plasma, additional experimental information is required. Although in the case of a rapidly recombining plasma the upper quantum states of the radiative transitions are easily populated, the problem remains about the mechanisms and rates of depopulation of the lower states of the radiative transitions,  $C_2(a^3\Pi_u)$  and  $C(2p^2, ^1S_0)$ . Optical transitions from these states to lower-lying states are forbidden [8]. This means that only collisional depopulation has to be considered. The following mechanisms of

collisional quenching of these states can be suggested. For the state  $C_2(a^3\Pi_u, v'', j'')$  it is collisional depopulation to the ground state  $C_2(X^1\Sigma_g^+, v^0, j^0)$ . These reactions must be very fast [1], since the energy gap between the states is only  $\Delta E \approx 0.09$  eV, which is smaller than the translational energy of the particles in the plasmas. For the quenching of the atomic carbon excited state  $C(2p^2, ^1S_0)$  a very fast reaction might be quasi-resonant excitation exchange collisions with the ground state carbon atoms:  $C(2p^2, ^3P_0) + C(2p^2, ^1S_0) \rightarrow C(2p^2, ^1D_1) + C(2p^2, ^1D_1)$  (positive excess of energy  $\Delta E \approx 0.15$  eV). Another additional reason for the depopulation of the lower quantum states  $C_2$  and C might be fast clustering, which, as has been shown [11], is very effective in expanding plasmas.

#### Acknowledgements

This work has been supported by the Netherlands Foundation for Fundamental Research (FOM). The research of M.C.M. van de Sanden has been made possible by the Royal Netherlands Academy of Arts and Sciences. The authors wish to thank M.J.F. van de Sande, A.B.M. Hüsken and H.M.M. de Jong for their skilful technical assistance.

#### References

- [1] L.I. Gudzenko and L.A. Shelepin, *Sov. Phys. — JETP*, 18 (1964) 988.
- [2] S.W. Bowen and C. Park, *AIAA J.*, 10 (1972) 522.
- [3] T. Hara, K. Kodera, M. Hamagaki, K. Matsunaga, M. Inutake and T. Dote, *Jpn. J. Appl. Phys.*, 19 (1980) L386.
- [4] M.C.M. van de Sanden, J.M. de Regt and D.C. Schram, *Phys. Rev. E*, 47 (1993) 2792.
- [5] A.J.M. Buuron, D.K. Otorbaev, M.C.M. van de Sanden and D.C. Schram, *Phys. Rev. E*, in press.
- [6] M.C.M. van de Sanden, G.M. Janssen, J.M. de Regt, D.C. Schram, J.A.M. van der Mullen and B. van der Sijde, *Rev. Sci. Instrum.*, 63 (1992) 3369.
- [7] A.C.G. Mitchell and M.W. Zemansky, *Resonance Radiation and Excited Atoms*, Cambridge University Press, Cambridge, 1971.
- [8] W.L. Wiese, M.W. Glennon and B.M. Smith, *Atomic Transition Probabilities*, NSRDS-NBS 4, Washington, DC, 1966.
- [9] L.L. Danylewich and R.W. Nicholls, *Proc. R. Soc. London Ser. A*, 338 (1974) 197.
- [10] V.N. Ochkin, S.Yu. Savinov and N.N. Sobolev, in N.N. Sobolev (ed.), *Electron-Excited Molecules in Nonequilibrium Plasma*, Nova, New York, 1989, p. 7.
- [11] B.M. Smirnov, *Plasma Chem. Plasma Proc.*, 13 (1993) 673.