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Absorption and stimulated emission between the electronic states of C and C₂ radicals in an expanding thermal plasma

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Abstract. Using the method of reabsorption the absolute densities of argon, atomic and molecular carbon are determined during the deposition of amorphous hydrogenated (diamond-like) carbon coatings by an expanding thermal arc plasma. Depending on the gas mixture argon/methane or argon/acetylene and the manner of hydrocarbon injection, the stationary negative or positive absorption between the quantum states $\text{Ar}(3p^5 4p \rightarrow 3p^5 4s)$, $\text{C}(2p^3 s \rightarrow 2p^2)$ and $\text{C}_2(d^3 \Pi_g, v' = 0 \rightarrow a^3 \Pi_u, v'' = 0)$ were obtained. From the line absorption the absolute population densities of the radicals in the plasma have been determined. The density of the argon first excited state $\text{Ar}(3p^5 4s, ^3P_2)$ is $\approx 10^{16} - 10^{17} \text{ m}^{-3}$, the atomic and diatomic molecular carbon densities are of the order of $10^{18} - 10^{19} \text{ m}^{-3}$.

In recombining plasmas the atomic and molecular excited states are populated by the recombining flux of particles going from the ionized states to the ground electronic state of the neutrals. In this situation the conditions favourable for the population inversion between quantum states can occur. This phenomenon, known as an amplification in a recombining plasma, has been predicted theoretically [1, 2] and demonstrated experimentally for the transitions between the excited states of various atoms [3–5]. In this paper absorption spectroscopy has been applied to measure the absolute densities of C and C₂ radicals during the deposition of amorphous hydrogenated carbon coatings by an expanding thermal arc plasma. A stationary population inversion between the electronic quantum states of the C₂ molecule is observed for the first time.

The measurements are carried out in the expanding thermal plasma produced by a cascaded arc, described in detail elsewhere [6–8]. 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 sub-atmospheric pressure $\approx 5 \times 10^4 \text{ Pa}$. This plasma expands into a low-pressure vessel through a conically shaped nozzle. Hydrocarbons (CH₄ or C₂H₂) are injected either at the end of the arc channel (nozzle), or in the early expansion. By means of charge exchange and subsequent dissociative recombination a beam of ionized and excited particles (Ar^{*+} , $(\text{C}_x\text{H}_y)^{*+}$, C_n^{*+} , H_m^{*+})

is created. The particles from the arc are accelerated to supersonic velocities of up to 4000 m s^{-1} , pass through a shock and are transported further at subsonic velocities. For typical pressures in the vessel of about 10^2 Pa the shock is observed at about 40 mm from the nozzle [7–9]. The plasma conditions under which the experiments have been performed are the following: background pressure 20–200 Pa, argon flow rate 58–116 scc s⁻¹, hydrocarbon flow rate 3–6 scc s⁻¹, arc current 45 A, arc voltage 70–80 V.

The measurements of the spectral line intensities are performed by the optical system presented in figure 1. As shown in the figure it consists of one concave mirror, and a system of a plane mirrors and lenses. The measurements are made 20 and 70 mm downstream of the arc nozzle, perpendicularly to the axis of the expanding plasmas. The detection section consists of a high-resolution monochromator with a focal length of 1 m and grating with 1200 lines per mm, and a Peltier cooled photodiode array. With this section a spectral range of $\approx 20 \text{ nm}$ with a resolution of 0.02 nm can be covered simultaneously. The optical system was calibrated positioning a tungsten ribbon lamp in the vessel, and recording the spectrum at a known true temperature of the ribbon.

The absorption or stimulated emission between the quantum states can be observed by measuring the apparent absorption coefficient of the spectral lines. An idea of optical absorption spectroscopy consists of the experimental determination of an integral absorption

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Figure 1. Outline of expanding cascaded arc plasma and absorption spectroscopy set-up. CAS_p, plasma source (cascaded arc); EP, expanding plasma; SS, substrate support; W, window; T, translator; C, rotating chopper; B, beamsplitter; F, order filter; CAS_i, external light source (cascaded arc); L1–L5, lenses; M1–M6, mirrors; P1–P2, diaphragms; MC, monochromator; PDA, photodiode array; PM, photomultiplier; PC, personal computer.

coefficient $\int_0^\infty k_\nu d\nu$, which for a homogeneous medium is equivalent to [10]:

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

where k_ν is the absorption coefficient, which is positive for absorption and negative for the stimulated emission, n_i and n_k are the total population densities of the particles on lower and upper quantum levels of the radiative transition, g_i and g_k their respective statistical weights, A_{ki} is the transition probability for spontaneous emission, and λ_0 is the central line wavelength.

For the determination of the absorption coefficient k_ν , the method of reabsorption with a mirror (which is identical to the method of two identical light sources [10, 11]) has been used. A concave mirror ($f = 25$ cm) of reflectance r was placed behind the plasma (see figure 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:

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

where ΔI is the absorbed radiation and I_1 and I_2 are the radiation from the plasma with covered and open mirror respectively.

In the case of radiative transport of a single spectral line the relation between A_L and absorption coefficient k_v is given by [10, 11]:

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

where l is the length of the light column. A_L as a function of k_v is presented, for example, in [10, 11]. When $A_L > 0$ absorption takes place, and the absolute density of the lower state of the transition can be derived from known A_L values. If $A_L < 0$, a population inversion is present, and the density of the upper state of the transition can be determined.

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

In order to check the validity of the discussed method it was first applied to measure the argon density in the first excited state Ar(3p⁵4s). The measurements were performed for a pure argon plasma at a distance of $x = 70$ mm from the nozzle of the arc. The gas flow rate was 58 scc s⁻¹, pressure in the vessel 40 Pa. For this condition the Ar(3p⁵4s) density was recently accurately measured using an external bright light source [8]. The absorption of the spectral line $\lambda = 696.5$ nm (radiative transition Ar(3p⁵4p $\rightarrow$ 3p⁵4s)) is used to determine the absolute density of Ar(3p⁵4s, ³P₂) state. To the same spectral range belongs another argon spectral line ($\lambda = 693.8$ nm) which is, however, a result of the radiative transition Ar(3p⁵4d $\rightarrow$ 3p⁵4p). From the absolute intensity of the spectral line $\lambda = 696.5$ nm, the absolute density of Ar(3p⁵4p) state has been determined. The measured density $n_{\text{Ar}(4p)} \simeq 5 \times 10^{13}$ m⁻³ was in a good agreement with the previously reported results [7].

Simple 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 $\lambda = 693.8$ nm. Therefore, the radiation of this line is used to measure the reflectance coefficient of the concave mirror. A value of $r = 0.65 \pm 0.03$ at $\lambda = 693.8$ nm was found. The measured value of the line absorption function A_L for $\lambda = 696.5$ nm for pure argon is shown in table 1.

Typical parameters for these plasma settings are $n_e \simeq 3 \times 10^{19}$ m⁻³, $T_e \simeq 3000$ K, and $n_0 \simeq 5 \times 10^{20}$ m⁻³ [7, 9] as measured using Thomson-Rayleigh scattering. The Voigt parameter $a \ll 1$, so that the Doppler limit (with the heavy particle temperature $T_0 \simeq 3000$ K [7, 8]) for the Voigt function applies. The characteristic value for the absorption length has been derived from the lateral profile of the emissivity of the line $\lambda = 693.8$ nm. For the condition mentioned it was found that $l = 35$ mm (see also [8]).

Finally, using equations (1) and (3), and measured A_L values for the line $\lambda = 696.5$ nm, the averaged absolute density of the Ar(3p⁵4s, ³P₂) state is $n_{\text{Ar}(4s)} \simeq 2 \times 10^{17}$ m⁻³. This value is in good agreement with detailed measurements of Buuron *et al* [8]. It clearly indicates that the discussed procedure using the concave mirror is a simple but effective experimental method. 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 accuracy of the discussed procedure is limited by the errors during the measurements of r and A_L . We estimate the error in the density determination by the discussed method to be within a factor of two.

To measure the C₂ molecule density in the expanding plasma the well known Swan system of C₂ (d³Π_g, $v' = 0 \rightarrow a^3$ Π_u, $v'' = 0$ transition, band head at $\lambda = 516.5$ nm) has been used. To the same spectral range belong two spectral lines of argon:

$\lambda_1 = 516.2$ nm (radiative transition Ar(3p⁵6d $\rightarrow$ 3p⁵4p))

and

$\lambda_2 = 518.8$ nm (radiative transition Ar(3p⁵5d $\rightarrow$ 3p⁵4p)).

Table 1. Experimental conditions and measured values of absorption function A_L for the argon line $\lambda = 696.5$ nm (3p⁵4p $\rightarrow$ 3p⁵4s transition), and for the band head of the Swan system of C₂ (d³Π_g, $v' = 0 \rightarrow a^3$ Π_u, $v'' = 0$ transition).

Gas mixture	Flow rate (scc s ⁻¹)	C _x H _y injection	Axial position (mm)	Pressure (Pa)	A_L
Ar	58	—	70	40	+0.29
CH ₄ /Ar(1:20)	61	nozzle	70	50	-0.25
CH ₄ /Ar(1:20)	61	nozzle	70	100	-0.36
CH ₄ /Ar(1:20)	61	nozzle	70	200	-0.30
CH ₄ /Ar(1:40)	119	nozzle	70	100	-0.17
CH ₄ /Ar(1:10)	64	nozzle	70	100	-0.55
CH ₄ /Ar(1:20)	61	vessel	70	100	-0.06
C ₂ H ₂ /Ar(1:20)	61	nozzle	70	100	+0.16
C ₂ H ₂ /Ar(1:20)	61	vessel	70	100	+0.10
CH ₄ /Ar(1:20)	61	nozzle	20	100	0

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 [12]. Therefore these transitions are also optically transparent, 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 $r = 0.74 \pm 0.04$.

For different experimental conditions the A_L values 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) in both argon/methane and argon/acetylene plasmas are shown in table 1. As can be seen for all the conditions with methane injection into the reactor, at the axial position of $x = 70$ mm, i.e. in the subsonic part of the expansion, a negative absorption takes place (A_L is negative). The effect is more pronounced for injection in the nozzle and larger methane admixtures. Absorption is absent at the position $x = 20$ mm, and is positive, when the acetylene was injected into the reactor.

In the experimental conditions the Voigt parameter for the rovibronic spectral lines of the Swan system $a \ll 1$, and again the Doppler limit (with the temperature $T \approx 3000$ K [7, 8]) for the Voigt function applies. The absolute transition probabilities, the Franck-Condon and the Hönl-London factors for the Swan bands, needed for the calculation of C_2 densities from the spectral line intensities, were taken from the literature [13]. The values for the absorption length in various plasma conditions were derived by a lateral scanning of the spectral lines emissivities.

The negative values of A_L give fairly large population inversions. The total density of the excited $C_2(d^3\Pi_g, v'=0)$ molecules for the experimental conditions, presented in table 1, give $n_{C_2(d^3\Pi)}$ densities in the range from $2 \times 10^{18} \text{ m}^{-3}$ up to $1.5 \times 10^{19} \text{ m}^{-3}$. Overlapped molecular spectral line absorption has been treated as in the literature [10, 14]. 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 was injected into the reactor the absorption was 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 to $5 \times 10^{18} \text{ m}^{-3}$. Note, however, that the measured A_L values, as well as the molecular densities are averaged across the plasma beam, and the local absolute values for the absorption function and for the densities may be even larger.

In the supersonic part of the expansion (axial position $x = 20$ mm) $A_L = 0$, as is seen from table 1. This means that either the density of states is small enough, i.e. the absorption signal is below the detection limit, or the densities of upper and lower states are large but equal (or comparable) to each other (see equation (1)). A major difference between the injections of methane and acetylene to the reactor is the sign of A_L (see table 1). As an explanation it seems reasonable to assume that with the acetylene injection in 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 and H_2 , which gives positive absorption.

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

In the subsonic part of the expansion, when the total gas flow rate was 61 scc s^{-1} , and methane ($CH_4/Ar = (1:20)$) was injected into the nozzle of the arc, the A_L values for atomic carbon were always negative from $A_L = -0.16$ (at $p = 50$ Pa) to $A_L = -0.88$ (at $p = 200$ Pa). Using the same calculation procedure as for C_2 , the atomic carbon absolute density in the excited state $C(2p3s, ^1P_1)$ can be estimated. Averaged across the plasma beam, the densities were in the range of $n_C = (2-9) \times 10^{18} \text{ m}^{-3}$. These $C(2p3s, ^1P_1)$ atom densities are of the same order of magnitude as measured in the free-jet stream produced in a constricted arc [4].

In order to understand the 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, a question remains about the mechanisms and efficiency of depopulation of the lower states of radiative transitions: $C_2(a^3\Pi_u)$ and $C(2p^2, ^1S_0)$. The radiative transitions from these states to lower lying states are forbidden [12]. Therefore only collisional quenching has to be considered. The following mechanisms of collisional depopulation of these states can be suggested. For the state $C_2(a^3\Pi_u, v'', j'')$, collisional quenching to the ground state $C_2(X^1\Sigma_g^+, v^0, j^0)$ is considered. These reactions are very effective [2], since the energy gap between the states is only $\Delta E \approx 0.09$ eV and 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 effective channel is the 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 of C_2 and C might be fast clustering which, as has been shown [15, 16], is very effective in expanding plasmas.

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References

- [1] Gudzenko L I and Shelepin L A 1964 *Sov. Phys. JETP* **18** 998
- [2] Gudzenko L I, Shelepin L A and Yakovlenko 1975 *Sov. Phys. Uspechi* **17** 848
- [3] Goldfarb V M, Ilina E V, Kostygova I E and Lukyanov G A 1968 *Opt. Spectrosc.* **27** 108
- [4] Bowen S W and Park C 1972 *AIAA J.* **10** 522
- [5] Hara T, Kodera K, Hamagaki M, Matsunaga K, Inutake M and Dote T 1980 *Japan. J. Appl. Phys.* **19** L386
- [6] Kroesen G M W, Timmermans C J and Schram D C 1988 *Pure Appl. Chem.* **60** 795
- [7] van de Sanden M C M, de Regt J M and Schram D C 1993 *Phys. Rev. E* **47** 2792
- [8] Buuron A J M, Otorbaev D K, van de Sanden M C M and Schram D C 1994 *Phys. Rev. E* **50** 1383
- [9] van de Sanden M C M, Janssen G M, de Regt J M, Schram D C, van der Mullen J A M and van der Sijde B 1992 *Rev. Sci. Instrum.* **63** 3369
- [10] Mitchell A C G and Zemansky M W 1971 *Resonance Radiation and Excited Atoms* (Cambridge: Cambridge University Press)
- [11] Frish S E 1970 *Spectroscopy of Gas Discharge Plasmas* (Leningrad: Nauka)
- [12] Wiese W L, Glennon M W and Smith B M 1966 *Atomic Transition Probabilities* (Washington, DC: NSRDS-NBS 4)
- [13] Danylewicz L L and Nicholls R W 1974 *Proc. R. Soc. A.* **338** 197
- [14] Ochkin V N, Savinov S Yu and Sobolev N N (ed) 1989 *Electron-Excited Molecules in Nonequilibrium Plasma* (New York: Nova Science) p 7
- [15] Huq S E, McMahon R A and Ahmed H 1990 *Semicond. Sci. Technol.* **5** 771
- [16] Smirnov B M 1993 *Plasma Chem. Plasma Proc.* **13** 673