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

ABSORPTION AND STIMULATED EMISSION BETWEEN THE ELECTRONIC STATES OF C AND C_2 RADICALS IN AN EXPANDING THERMAL PLASMA

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In a recombining plasmas the atomic and molecular excited states are populated by the flux of particles going from the ionized states to the ground electronic state of the neutrals. In this situation the conditions favorable for the population inversion between quantum states can occur. In this paper absorption spectroscopy has been applied to measure the absolute densities of C and C_2 radicals during the deposition of carbon coatings by an expanding thermal arc plasma. A stationary population inversion between the electronic quantum states of the C_2 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 [1]. In the cascaded arc a thermal plasma in argon is created in a cylindrical channel. This plasma expands into a low pressure vessel through a conically shaped nozzle. 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, hydrocarbons are injected either at the end of the arc channel (nozzle), or directly into the vessel with flow rate 3 - 6 scc/s, arc current 45 A, arc voltage 70 - 80 V. The measurements of the spectral line intensities are performed by the optical system, which consists of one reflective concave mirror, and a system of a plane mirrors and lenses. To measure the density of the states a method of reabsorption with a mirror (which is identical to the method of two identical light sources [2]) have been used. For the determination of the line absorption function A_L [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.

The method was first applied to measure the argon density in the first excited state Ar($3p^5 4s$) in a pure argon plasmas. In the similar condition the Ar($3p^5 4s$) density was recently accurately measured using an external bright light source [3]. The absorption of the spectral line $\lambda = 696.5$ nm (Ar($3p^5 4p \rightarrow 3p^5 4s$)) is used to determine the absolute density of Ar($3p^5 4s$, $^3P_2$) state. The averaged over the plasma cross section absolute density of the Ar($3p^5 4s$, $^3P_2$) state is $n_{Ar(4s)} \simeq 2 \cdot 10^{17}$ m^{-3}. This value is in good agreement with detailed measurements of Buuron et. al. [3].

To measure the C_2 molecules density in the expanding plasma the Swan system of C_2 ($d^3\Pi_g, v' = 0 \rightarrow a^3\Pi_u, v'' = 0$ transition) has been used. The values of line absorption function A_L [2] 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. As can be seen for all the conditions with methane injection into the reactor, a negative absorption takes place. 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, give $n_{C_2(d^3\Pi)}$ densities in the range from $2 \cdot 10^{18}$ m^{-3} up to $1.5 \cdot 10^{19}$ m^{-3}. Overlapped molecular spectral line absorption has been treated as in Ref. [2].

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, $n_{C_2(a^3\Pi)}$ was in the range 3 to 5 $\cdot 10^{18}$ 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. A major principal difference between the injections of methane and acelylene to the reactor is the sign of A_L. As an explanation it seems reasonable to assume that with the acetylene injection into the reactor, the direct collisional and/or thermal dissociation reaction: $C_2H_2 \rightarrow C_2 + H_2$, becomes most important. Probably this reaction mainly populates the low-lying electronic states of C_2 and H_2, which gives positive absorption.

Gas mixture	Flow rate (scc/s)	C_xH_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(1:20)	61	vessel	70	100	- 0.06
C_2H_2/Ar(1:20)	61	nozzle	70	100	+ 0.16
C_2H_2/Ar(1:20)	61	vessel	70	100	+ 0.10

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 $(C(2p3s,\ ^1P_1 \rightarrow 2p^2,\ ^1S_0))$. In order to measure the reflectance coefficient of the mirror, the same carbon line emission was used, but in a specific experimental regime, where the plasma is thought to be optically transparent for the radiation. Averaged across the plasma beam, the carbon density was in the range of $n_C = (2-9)\cdot 10^{18}$ m^{-3}.

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, more additional experimental information is required. Although in the case of rapidly recombining plasma the upper quantum states of the radiative transitions is easily populated, the question remains about the mechanisms and efficiency of depopulation of the lower states of radiative transitions: $C_2(a^3\Pi_u)$ and $C(2p^2,\ ^1S_0)$. Since the radiative transitions from these states to lower lying states are forbidden, the only collisional quenching has to be considered. 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 [4] is very effective in expanding plasmas.

References

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