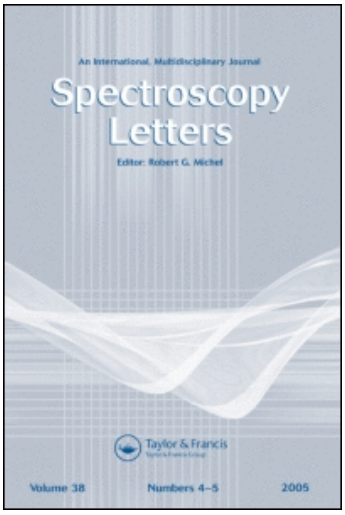

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SPECTROSCOPIC STUDY OF C_2 IN CARBON ARC DISCHARGE

Key words: C_2 spectroscopy, Swan system, self-absorption, carbon arc plasma,

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ABSTRACT

The influence of self-absorption on intensity distribution in the rotational structure of the emission d $^3\Pi_g \rightarrow$ a $^3\Pi_u$ (0-0) band of C_2 radical was studied. The self-absorption effect was used for the determination of C_2 concentration in a DC carbon arc. The proposed method is general and may be used to other molecular bands of a similar rotational structure.

INTRODUCTION

Great attention is being paid presently to the high current carbon arc plasma. This growing interest has been evoked by the discovery that the carbon arc discharge is the most effective source of fullerenes and carbon nanotubes [1,2]. The process is carried out usually under

medium helium pressure [1]. Surprisingly for such an important plasma source, a comprehensive and thorough experimental study has yet to be made, especially regarding the plasma characterization. Such a study should provide new insights into the fullerene formation mechanism, which has not been unambiguously identified so far. Up to now most of the available results have been of a rather qualitative character, e.g. some components of the plasma were detected and arc temperatures were estimated [3-6]. This is mostly due to considerable experimental difficulties in plasma quantitative diagnostics. These arise from the small interelectrode gap of the arc plasma, high fluctuation of the ablation processes and the necessity of a continuous movement of both electrodes to hold a small discharge gap (≈ 1 mm) in a given position relative to the optical detection axis.

The literature [3,4] and our [5,6] data showed that only few intermediate carbon species are detectable in the plasma zone using conventional emission or absorption techniques, in spite of complex C_n molecules in the gas phase [7] and C_{60} and higher carbon clusters found in the soot deposit.

In the UV and VIS radiation only carbon atomic CI (247.8 nm...) and ionic CII (392, 657 nm...) lines, and molecular bands of C_2 ($C\ ^1\Pi_g \rightarrow A\ ^1\Pi_u$, $d\ ^3\Pi_g \rightarrow a\ ^3\Pi_u$) are available for plasma diagnostics. Also helium atomic lines, mainly HeI (388.8 nm), are present in the emission spectrum. However, the intensity of HeI and CII lines decreases drastically with a discharge current increase and their total disappearance is observed above 70 A [5,6]. Thus the excited C_2 radicals and CI atoms become the main source of the radiation in the VIS and UV spectrum, respectively. One should mention that C_2 is considered as the main fullerene and nanotube precursor [8]. Hence, our interest in the quantitative determination of these radicals.

Intensity measurements of the radiation emitted from the arc plasma by C_2, mainly d $^3\Pi_g \rightarrow$ a $^3\Pi_u$ Swan system, have been reported in several papers but only rotational temperatures of excited C_2 were determined [3,5,6,9]. In our previous works related to an AC arc [5] the concentration of C_2 was estimated from the absolute intensity measurements of the 516.5 nm Swan (0,0) band. This work is a continuation of those studies. The aim was to elaborate a method of the determination of C_2 radicals density for a DC carbon arc when the electrode ablation rate, and consequently C_2 concentration, is high [5,10]. Since the band intensity distribution and its absolute value can be disturbed by self-absorption under such conditions this effect has to be taken into account whenever rotational temperatures or emission coefficients are to be determined. However, the self-absorption can be also used in the density determination of non-excited species, especially when strong plasma radiation makes difficult the application of conventional absorption techniques, i.e. the absorption in the background of a continuous spectrum. This is exactly the case of a high-current arc discharge. The influence of self-absorption on intensity distribution in the rotational structure of the d $^3\Pi_g \rightarrow$ a $^3\Pi_u$ (0-0) band was analyzed in detail and used for the C_2 (a $^3\Pi_g$, v=0) concentration determination in the plasma zone.

THEORY

The C_2 (0,0) Swan band was simulated for various optical densities and rotational temperatures. Afterwards the integrated band intensity of the normalized intensity distribution was obtained in a function of the volume density, i.e. the product of C_2 (a $^3\Pi_u$, v"=0) concentration and optical path length.

Spectrum Simulation: Low Optical Density

The method of calculation is based on the fundamental formula for the emission coefficient of the rotational components [11]:

$$\varepsilon_{J'J''} = \frac{2\pi he^2}{m} \nu^4 S_{J'J''} f_{mn} g_n q_{v'v''} \exp\left(-\frac{E'_J}{kT'_r}\right) Q_r'^{-1} N_{nv'}, \qquad 1$$

$$[W\ cm^{-3}\ sr^{-1}]$$

where T_r' is the rotational temperature of excited molecules, $S_{J'J''}$ are the H-L factors calculated according to Kovacs [12], $E_{J'}$ are the energies of the rotational levels J' from which the transitions originate (calculated according to Budo [13]), ν is the wavenumber, f_{mn} is the electronic absorption oscillator strength equal to 0.033 for Swan system [14], $g_n = 6$, $q_{v'v''}$ are the F-C factors equal to 0.722 and 0.333 for 0-0 and 1-1 bands, respectively [14] and $N_{mv'}$ is the population of the vibrational level v'(0 or 1) of the excited d $^3\Pi_g$ electronic state. The calculated spectrum of the individual rotational lines was convoluted with the apparatus function that in the case of our optical system was of Gaussian type with the width equal to 0.03 nm at half peak intensity. Fig.1 shows the spectrum simulated for $T_r' = 5500$ K (1) which contains the (0,0) and part of the adjacent (1,1) band.

Spectrum Simulation: Case of Self-Absorption

For an optically non-thin plasma the self-absorption has to be taken into account. This effect obviously depends on the absorption coefficient. The coefficient at a given frequency is a function of the volume density of absorbing molecules, real spectral line profile and the degree of overlapping of lines within their profiles.

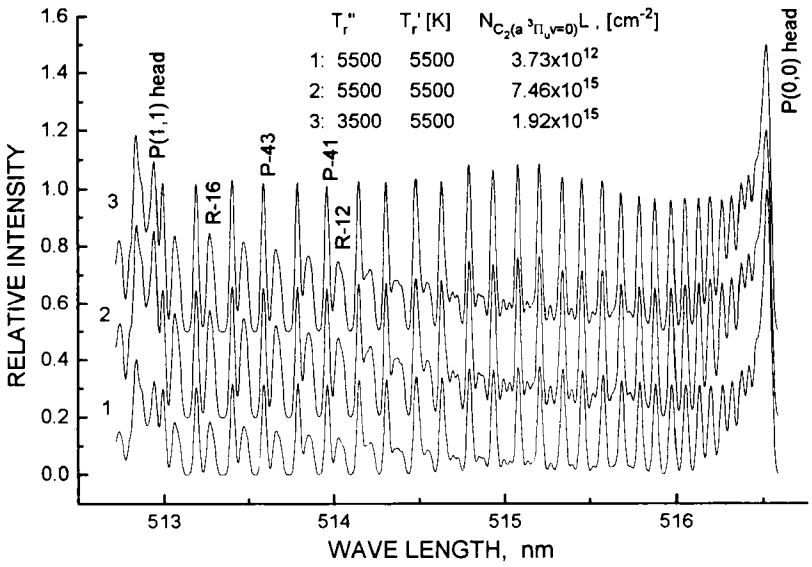

FIG. 1. Spectra of C_2 ($d\ ^3\Pi_g \rightarrow a\ ^3\Pi_u$) simulated for various volume densities.

When plasma is non-uniform (i.e. at high temperature gradients), transition from the observed intensity distributions to the local emission coefficients of the molecular bands (or vice versa in the case of spectrum simulation) is rather a complex task. In this work the calculations were done for the case of a uniform system only. The basic formula connecting the intensity of a rotational line with its emission coefficient for radiation emitted from a uniform plasma column of length L is as follows [15]:

$$I_{J'J''} = \int \frac{\varepsilon_{J'J''}(\nu)\,L}{\kappa(\nu)\,L}\,(1-e^{-\kappa(\nu)L})\,d\nu, \quad [W\,cm^{-2}\,sr^{-1}] \qquad (2)$$

where $\varepsilon_{J'J''}(\nu)$ and $\kappa(\nu)$ are the spectral line emission and absorption coefficients, respectively.

The total spectral absorption coefficient includes contributions from all possible transitions:

$$\kappa(\nu) = \sum \kappa_{J'J''}(\nu) \qquad 3$$

Because of high gas temperature and moderate carbon species pressure (a few kPa [6]) the calculations were performed assuming the Doppler broadening of the emission and absorption lines according to:

$$\varepsilon\,(or\ \kappa)_{J'J''}(\nu) = \varepsilon\,(or\ \kappa)^{o}_{J'J''} e^{-4\ln 2\left(\frac{\nu-\nu_{J'J''}}{\Delta\nu_D}\right)^2} \qquad 4$$

where $\varepsilon(\text{or } \kappa)^{o}_{J'J''}$ is the peak emission (or absorption) coefficient and $\Delta\nu_D$ is the Doppler width at half peak intensity. Assuming a statistical equilibrium between the rotational and translational degrees of freedom the Doppler width can be expressed by T_r' and T_r'' for the emission and absorption lines, respectively. Two different rotational temperatures reflect the situation when radiation from hot plasma zone is self-absorbed in the cooler region surrounding the emitting zone. The absorption coefficients in Eq. 2 are expressed by the concentration of C_2 radicals in the ground d $^3\Pi_u$ electronic state ($N_{mv''}$):

$$\kappa_{J'J''} = \frac{\pi e^2}{mc^2} f_{mn} q_{v'v''} S_{J'J''} e^{-\frac{E_J''}{kT_r''}} Q_r^{''-1} N_{mv''}, \quad [cm^{-2}] \qquad 5$$

The equations from 1 to 5 were used for the calculation of the spectra of individual rotational lines in a function of the volume density, N(a $^3\Pi_u$, v=0)xL, and rotational temperatures $T_r'$and T_r''. The examples of the spectral intensity distributions (normalized relatively to the P(0,0) head band) are shown in Fig. 1.

Method of $C_2(a\ ^3\Pi_u,\ v=0)$ Concentration Determination

The P(0,0) head band is the most sensitive part of the spectrum to the self-absorption because it contains many lines overlapping within their real profiles. As a result, with the volume density increasing there is a significant increase in the intensities of the resolved rotational components relative to the P(0,0) head band. This is clearly seen comparing the traces (1), (2) and (3) in Fig. 1. It can be quantitatively expressed by the integrated intensity of the normalized (0,0) band in a function of the volume density. The integration was made between the P(0,0) and P(1,1) head bands. Such dependance (called here growth curves) is illustrated by solid curves in Fig. 2. The integrated band intensities were expressed in arbitrary units related to the bands not disturbed by self-absorption at given rotational temperatures. Thus, the proposed method of the determination of C_2 concentration is based on such dependence. The volume density can be directly obtained from the growth curves after the experimental determinations of the integrated emission intensities from the normalized band intensity distributions. The knowledge of the absorbing column length (L) leads directly to the average radical concentration value; in the case of the axial symmetry it is also possible to obtain radial concentration distributions. From Fig. 2 it follows that self-absorption becomes significant at volume densities 10^{15} cm^{-2}. Hence, the intensity distribution 1 in Fig. 1 corresponds to the optically thin plasma and resembles the spectrum computed directly from the emission coefficients (Eq. 1).

When the integrated intensity in absolute units is considered (non-normalized spectrum), then one can see the opposite dependence on the volume density (Fig. 2 - dotted lines).

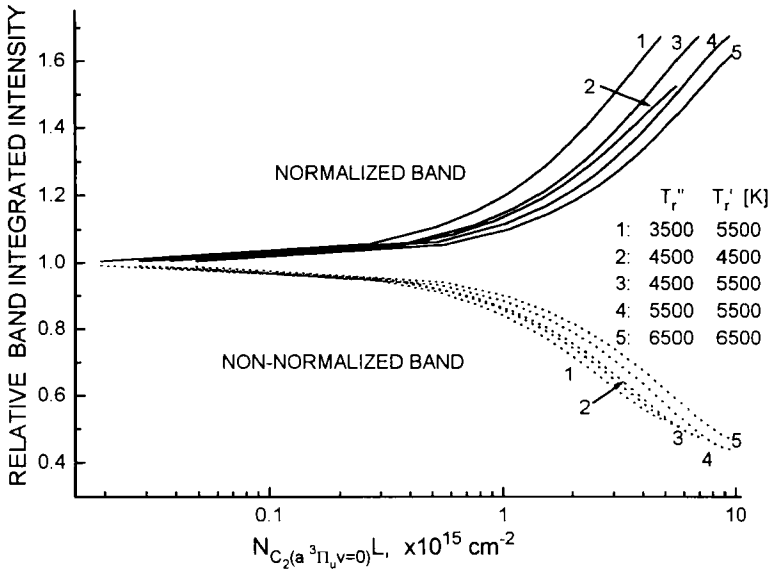

FIG. 2. Relative band integrated intensity of normalized and non-normalized C_2 (d $^3\Pi_g \rightarrow$ a $^3\Pi_u$) spectra vs. volume density.

Error in Rotational Temperature Determination

As the intensity distributions had already been obtained, it was of interest to inquire whether the rotational temperature could be directly determined from the Boltzmann plots $\ln(I/S\nu^4)$ vs. E'. Such a procedure was applied to the simulated spectra using lines with J′ between 26 and 30, and 39 and 45 of the P(0-0) branch [6]. The errors of the temperature calculations as a function of the volume density are presented in Fig. 3. The T_r'(calc) denotes the temperature calculated from the Boltzmann plots. As expected at low volume densities T_r'(calc) is close to T_r'. The temperature errors are also small when $T_r' \approx T_r''$ (around 5000 K - curves 1 and 4) for

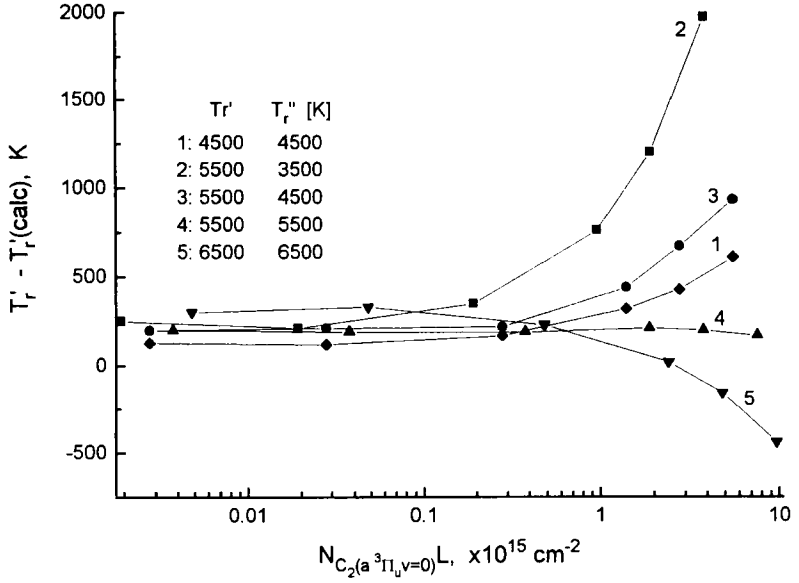

FIG. 3. Error in rotational temperature determination as a function of volume density.

low and high volume densities. Significant errors can be made when $T_r' > T_r''$(curve 2) when the calculated values can even be 2000 K overestimated.

EXPERIMENTAL

The spectroscopic arrangement consisted of a monochromator with the reciprocal dispersion of 0.6 nm mm^{-1}. A cylindrical cross section of the arc was twice magnified and imaged on the plane of the entrance slit of the monochromator. The height of the slit was reduced to 0.05 cm. The carbon electrodes were mounted in the horizontal position [6]. A plane and parallel rotating glass plate was placed between the entrance slit and a system of lenses. A digital photoelectronic system was used for

synchronization with the plate position acquisition data. The rotation axis was perpendicular to the slit, hence during a single C_2 spectrum scan distribution across the discharge gap could be simultaneously obtained. The center of the discharge gap of about 1 mm was held on the optical axis by an opto-electronic system that controlled the position of the electrodes during discharge.

RESULTS AND DISCUSSION

Examples of the normalized spectra recorded in the plasma center direction (y = 0) are shown in Fig. 4. The influence of self-absorption is clearly seen if one compares the intensity distributions for low (1) and high (2 and 3) arc currents. At low current (60 A) the intensity distribution is nearly undisturbed by the self-absorption. Due to some discrepancy between the calculated and real wavenumbers in the P(0,0) head band the relative intensities of the rotational components are even lower than those in the simulated spectrum 1 in Fig. 1. Therefore the experimental integrated intensity values of spectra affected by self-absorption were always considered relative to the experimental ones that were free of self-absorption.

The rotational temperatures determined from the Boltzmann plots are shown in Fig. 5. Since the temperature values on the edge of plasma (0.5 cm away from the center) were only a few hundreds K lower than those at the center the intensity distributions could be analyzed without application of the Abel inversion for sources of axial symmetry. Taking into account lower temperature and still significant self-absorption on the plasma edge as well as the conclusions from Fig. 3, one can say that the temperature values in Fig. 5 for i = 115 A rather overestimate the real ones. Of course, the temperatures can

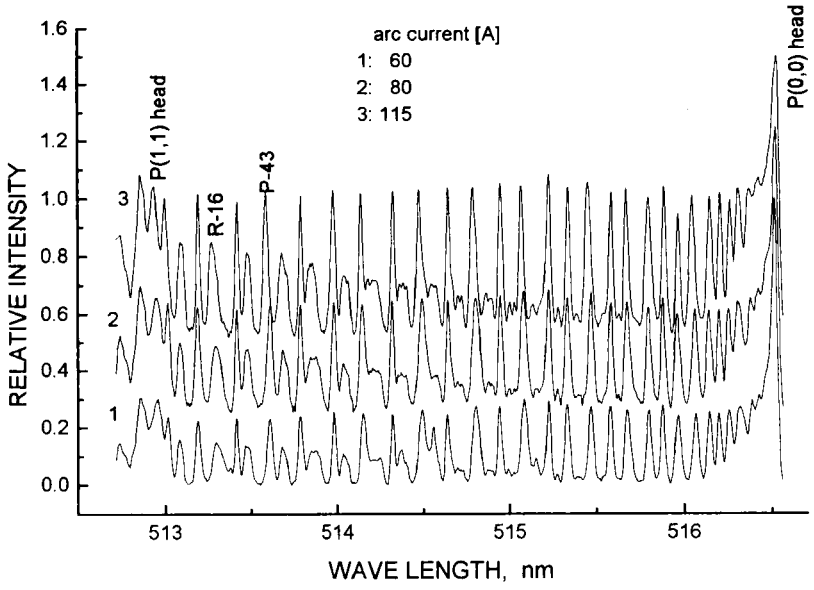

FIG. 4. Experimental spectra of C_2 (d $^3\Pi_g \rightarrow$ a $^3\Pi_u$) for various arc currents (y = 0).

not be lower then those obtained at lower current (60 A) when the effect of self-absorption was negligibly low. Therefore an arbitrary value of 5500 K was assumed as the average rotational (or gas) temperature of C_2 radicals in the arc gap. The gas temperature on the plasma edge is slightly higher than the electrode surface temperatures (being between 3000 and 4000 K [6,10]). Fig. 5 shows also the volume densities of C_2 (a $^3\Pi^u$,v=0) radicals at different horizontal positions (y) from the arc axis. The volume densities were read out from Fig. 2 (growth curve 4) using the experimentally determined values of the integrated band intensities of the normalized spectra. The axial symmetry allows in principle for the transition from the volume densities into the local C_2 (a $^3\Pi^u$,v=0)

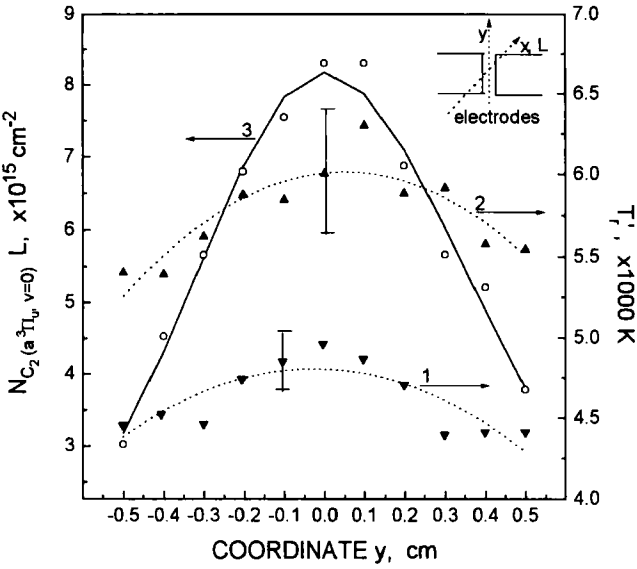

FIG. 5. Spatial distributions of volume densities of C_2 (a $^3\Pi_u$, v=0) and rotational temperatures. Arc current: 1 - 60 A; 2 and 3 - 115 A.

concentrations. However, it is apparent from Fig. 5 that absorption extends much further from the arc edge. Thus, the average concentration was estimated from the average volume density by subtracting the values at y = ± 0.5 cm. The obtained value $3x10^{15}$ cm^{-3} is of one factor higher than the in the case of the AC arc discharge ($2x10^{14}$ cm^{-3}) [6]. Such a distinct difference in C_2 (a $^3\Pi_u$, v=0) concentration in this study is related to much higher anode erosion rate at almost the same gas temperatures for DC and AC arc discharges.

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