Absolute concentration measurements of $C_2$ in a diamond CVD reactor by laser-induced fluorescence

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Abstract. By use of Laser-Induced Fluorescence (LIF) the absolute concentration of the $C_2$ radical in a microwave excited diamond chemical vapour deposition plasma has been measured for the first time. LIF spectra of the $d^3\Pi_u-a^3\Sigma_u^+$ (1, 0) Swan band near 473 nm were recorded and synthesized theoretically allowing the plasma temperature of 2100 $\pm$ 200 K to be inferred. Quenching rates were determined from time-resolved measurements of the fluorescence decay. By calibrating the LIF detection system, using spontaneous Raman scattering in $H_2$ in the reactor vessel, the absolute concentration of $C_2$ was determined to be $(7.5 \pm 1.7) \times 10^{10}$ cm$^{-3}$. Observations of the $C_2$ density under varying plasma conditions are reported.

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Low pressure microwave plasma Chemical Vapour Deposition (CVD) is a favoured technique for the production of high quality diamond films [1–4]. Although the quality of diamond films obtained with this method has constantly been improving in recent years, understanding of the fundamental chemical processes governing the deposition process is far from complete. One reason for this is the lack of experimental data which is required as input for chemical kinetics models. Theoretical models require detailed information of the concentrations of many chemical species present in the plasma environment. In particular one needs to know the spatial profiles and the variations of these concentrations as a function of parameter changes. Measuring the densities of many of the short-lived radicals important for diamond formation is a great experimental challenge. Their low densities and the extreme environment the plasma represents make their detection a difficult task.

This paper reports on what is believed to be the first quantitative measurement of $C_2$ concentrations in a low pressure diamond CVD reactor using Laser-Induced Fluorescence (LIF). $C_2$ is considered to be an important intermediate in the plasma environment [5] and has even been suggested as a possible growth species [6]. The importance of $C_2$ has recently been underlined by the observation that there is a strong correlation between the quality of the diamond films obtained and the quantity of $C_2$ present in the plasma [7].

LIF is a powerful, non-intrusive diagnostic technique offering high sensitivity and spatial resolution for the detection of minor species in hostile environments [8]. It has been successfully applied to measure the concentrations of short-lived radicals such as OH, $C_2$ and CH in atmospheric pressure flames [9, 10].

In low pressure systems concentrations of stable species could be successfully quantified by creating a calibration signal involving a known density of the species. On the other hand, absolute concentrations of transient species, such as OH, have also been determined in low pressure flames by cross-calibrating the LIF signal with absorption measurements. Measurements of NO and OH in a low pressure methane air flame (30–120 Torr) using these two techniques have been reported [11].

For most short-lived species present in a low pressure plasma, absorption is far too small to be measured directly. In this case some independent means of calibrating the LIF signal must be employed. In the present work calibration was achieved by use of spontaneous Raman scattering in $H_2$ following the method of Bischel [12].

1 LIF concentration measurements

In LIF, population is transferred from a ground state to an excited state during the laser pulse. The excited molecules relax to the available lower states. Some of these molecular transitions result in the emission of fluorescence photons. This induced fluorescence constitutes the LIF signal and is collected with a suitable light detection system. The number of photons emitted may be related to the population density of the absorbing species. For a quantitative measurement one has to take account of molecular collisions which can lead to population transfer back to the ground state without fluorescence being
emitted (quenching). It is equally important to know the efficiency of the fluorescence collection system and a calibration experiment is required to relate the LIF signal to an absolute number of photons emitted from the interaction region.

Quenching effects can in principle be overcome by using saturated LIF where the signal becomes independent of both laser power and collisions. However, proper application of this technique is very difficult because equal degrees of saturation cannot be achieved at all points of the interaction volume. For the present work it was decided to work in the unsaturated regime where the LIF signal is linear with laser energy. This requires knowledge of the quenching rates which were measured directly under similar experimental conditions.

Several methods have been employed for calibration of a fluorescence collection system. In one method laser light of the same wavelength as the LIF signal is scattered off a ground quartz disk placed at the interaction region. The interaction region is imaged by the same light collection system as the LIF signals and the same detection electronics are employed [13]. The signal thus created can be related to an absolute number of photons originating from the quartz disk. A problem with this method is that it is very difficult to relate the scattering geometry to the interaction volume of the corresponding LIF experiment.

A different method employs spontaneous Rayleigh scattering at the LIF emission wavelength created in a known concentration of a species with a known scattering cross-section [14, 15]. Here the interaction geometries match very well. However, the Rayleigh signal occurs at the laser wavelength and discrimination against laser scatter from windows and optical components is often not possible.

Bischel et al. [12] devised a calibration technique that is very similar in nature to the Rayleigh technique but is based on spontaneous Raman scattering in H₂. It offers the advantages of the former method with the additional advantage that the laser and signal wavelengths are well separated. Discrimination of the Raman signal is thus easily achieved. The spectroscopy of H₂ is very well understood and the Raman cross-sections for this molecule are accurately known. For these reasons spontaneous Raman scattering was an ideal candidate for accurate calibration of the LIF experiments described in this paper. Prior to a concentration measurement the reactor was simply filled with a few hundred Torr of room temperature H₂. The dye laser was tuned to the appropriate shorter wavelength to produce a Raman signal at the LIF emission wavelength. Beam geometry and detection system were exactly matched to the corresponding LIF experiment. The Raman signals were observed as a function of H₂ pressure and the resulting graph led to a calibration constant from which a LIF signal could be related to an absolute number of photons emitted from the interaction region.

## 2 Theory

The number of molecules $N_2$ transferred into the excited state during a laser pulse is given by [16]

$$N_2 = N_{10} \frac{B_{12}}{B_{12} + B_{21}} \frac{1}{1 + I_{sat}/I_o},$$

(1)

where $N_{10}$ is the ground state population prior to excitation by the laser pulse. $B_{12}$ and $B_{21}$ are the Einstein coefficients for stimulated absorption and stimulated emission respectively. $I_o$ is the spectral laser intensity (in W cm⁻² Hz⁻¹) and the saturation intensity $I_{sat}$ is defined as

$$I_{sat} = \frac{(A_{21} + Q_{21})c}{B_{12} + B_{21}},$$

(2)

where $A_{21}$ is the rate of spontaneous emission and $Q_{21}$ is the collision-induced quenching rate. Equation (1) assumes that the system has reached steady state during the laser pulse. In saturated LIF one operates at $I_o \gg I_{sat}$. In this regime $N_2$ becomes independent of both laser power and quenching effects [17]. It can be seen that the fluorescence signal is a maximum at saturation. For these reasons saturated LIF is a useful technique for radical concentration measurements [18, 19]. However, several authors have pointed out pitfalls that can lead to large errors in concentration measurements when using saturated LIF. Complete spatial saturation cannot be achieved because of the intensity variation across the laser beam; in the wings of the laser beam profile the laser intensity falls off and quenching effects cannot be neglected in these regions [13]. Several models have been developed to account for these effects [20]. The spatial variation of the degree of saturation affects the local population dynamics and different rate equations may apply at different points within the interaction volume. The result is that temporal saturation may not occur simultaneously in all regions of the probe volume [21]. Neglect of these wing effects can lead to errors in magnitude larger than the measured concentration [22]. A method to eliminate the contributions from the lateral regions of the probe volume has been suggested by Salmon and Laurendau [15]. This method uses only the saturated fluorescence emitted along the axis of the laser beam. For a radially symmetric intensity profile this centre line fluorescence can be extracted from the lateral fluorescence profile by use of an Abel transformation [23]. The lateral profile of the fluorescence volume can be measured by scanning the image of the fluorescence volume across a narrow slit placed in the image plane of the fluorescence collection system. Since a large fraction of the signal is lost in this method high signal levels are needed to allow quantitative measurements with this technique.

In the present work $I_o$ was below or only slightly above $I_{sat}$ to avoid the wing effects described above. Work in this regime requires knowledge of the quenching rate $Q_{21}$. A disadvantage is that errors in $Q_{21}$ are carried over linearly into the concentration determination. This is the major reason why saturated LIF is the preferred method in atmospheric pressure application where quenching collisions dominate the population dynamics and cannot be measured directly [9]. However, the microwave plasma operates at moderate pressures (between 40 and 80 Torr) and this makes it possible to measure the decay rate of the fluorescence signal from which $Q_{21}$ is obtained. Typical fluorescence decay times in the plasma were between 20 and 30 ns and could be determined to better than 1.5 ns.