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Optical emission spectroscopic study of plasma plumes generated by IR CO2 pulsed laser on carbon targets

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Abstract
Optical emission spectroscopy studies, in the spectral range ultraviolet–visible–near infrared (UV–Vis–NIR), were performed to investigate thermal and dynamical properties of a plume produced by laser ablation of a graphite target. Ablation is carried out using a high-power IR CO2 pulsed laser at \( \lambda = 9.621 \) \( \mu \)m, power density ranging from 0.22 to 5.36 GW cm\(^{-2}\) and air pressures around 4 Pa. The strong emission observed in the plasma region is mainly due to electronic relaxation of excited C, ionic fragments C\(^+\), C\(^{2+}\) and C\(^{3+}\) and molecular features of C\(_2\)(d\(^3\)\(\Pi_g\)–a\(^3\)\(\Pi_u\); Swan band system). The medium-weak emission is mainly due to excited atomic N, H, O, ionic fragment C\(^{4+}\) and molecular features of C\(_2\)(E\(^1\)\(\Sigma_g^+\)+–A\(^1\)\(\Pi_u\); Freymark system), C\(_2\)(C\(^2\)\(\Sigma_g^+\)+–X\(^2\)\(\Pi_u\); Deslandres–d’Azambuja system), OH(A\(^2\)\(\Sigma_g^+\)+–X\(^2\)\(\Pi_u\)), CH(A\(^2\)\(\Delta_g\)+–X\(^2\)\(\Pi_u\)); Phillips system) and CN(A\(^2\)\(\Pi_g\)+–X\(^2\)\(\Pi_u\); red system). An excitation temperature \( T_{\text{exc}} = 23,000 \pm 1900 \) K and electron densities in the range (0.6–5.6) \( \times 10^{16} \) cm\(^{-3}\) were estimated by means of C\(^+\) ionic lines. The characteristics of the spectral emission intensities from different species have been investigated as functions of the ambient pressure and laser irradiance. Estimates of vibrational temperatures of C\(_2\) and CN electronically excited species under various laser irradiance conditions are made.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon materials such as graphite, diamond, fullerenes, carbon nanofibres and carbon nanotubes are promising as electronics components, scanning probes, hydrogen storage and field emitters. So far, the growth of diamond, carbon nanofibres and carbon nanotubes has been performed mostly through chemical vapour deposition (CVD), arc discharge and laser ablation methods [1–6]. Pulsed laser ablation (PLA) provides a means of depositing thin coatings, of a wide range of substrates, at room temperature. Diamond-like carbon (DLC) thin films have attracted a considerable amount of scientific interest in the field of electronic research due to their outstanding properties, such as high hardness, chemical inertness, high thermal conductivity, high electrical resistivity and optical transparency from UV to IR [7]. For the production of high-quality DLC films through PLA, it is necessary to understand the formation of atomic and molecular species and their dependence on various parameters such as the laser power density, pressure of the boundary ambient atmosphere, concentration of the species at different distances from the target and so forth. Despite its versatility and wide applicability, however, many aspects of the detailed chemical physics underlying the ablation process are still far from completely understood. The process is often envisaged as a
sequence of steps, initiated by the laser radiation interacting with the solid target, absorption of energy and localized heating of the surface and subsequent material evaporation. The properties and composition of the ablation plume may evolve, both as a result of collisions between particles in the plume and through plume–laser radiation interactions. The laser–target interactions will be sensitively dependent both on the nature and condition of the target material and on the laser pulse parameters. Subsequent laser–plume interactions will also be dependent on the properties of the laser radiation, while the evolution and propagation of the plume will also be sensitive to collisions and thus to the quality of the vacuum under which the ablation is conducted and/or the presence of any background gas. Obviously, the ultimate composition and velocity distribution of the ejected material is likely to be reflected in the detailed characteristics of any deposited film.

Optical emission spectroscopy (OES) is a powerful tool to get information on the laser-ablated species. For laser ablation of carbon, OES studies in different atmospheres are reported and these studies have yielded many interesting results [8–31]. Detailed studies of laser-induced breakdown spectroscopy on N2 and SiH4 in the gas phase have been recently made in our laboratory [32, 33].

In this work, OES has been used to investigate thermal and dynamical properties of a plume produced by laser ablation of a graphite target at air pressures around 4 Pa. Ablation is performed using a high-power IR CO2 pulsed laser. The emission generated by the plasma in the spectral region 200–1100 nm is due to electronic relaxation of excited C, N, H, O, ionic fragments C+, C2+, C3+, C4+, and molecular features of C2(E1Sigma1–A1Pi0; Freymark system), C2(D1Sigma1–X1Sigma1; Mulliken system), CN(D2Pi–A2Pi), C2(e3Pi–g3Pi; Fox–Herzberg system), C2(C1Pi–A1Pi; Deslandres–d’Azambuja system), OH(A2Sigma1–X2Pi), CH(C2Sigma1–X2Pi), NH(A3Pi–X3Sigma1), CN(B2Sigma1–X2Sigma1; violet system), C2(d3Pi–g3Pi; Swan band system), CH(B2Sigma1–X2Pi), CH(A2Delta–X2Pi), C2(A1Pi–X1Sigma1; Phillips system) and CN(A2Pi–X2Sigma1; red system). As far as we know, a spectrum so rich in atomic lines belonging to ionized species and molecular features has not been previously observed in similar experiments. The excitation temperature and electron densities were obtained from C+ ionic lines. We have also studied here the spectral emission intensities from different species as functions of the ambient pressure and laser irradiance. Estimates of vibrational temperatures of C2 and CN electronically excited species under various laser irradiance conditions are reported.

2. Experimental

2.1. Experimental details

The schematic diagram of the experimental setup is shown in figure 1. A transverse excitation atmospheric (TEA) CO2 laser (Lumonics model K-103) operating on an 8 : 8 : 84 mixture of CO2 : N2 : He, respectively, was employed to ablate a graphite target. The laser is equipped with frontal Ge multimode optics (35% reflectivity) and a rear diffraction grating with 135 lines mm−1 blazed at 10.6 µm. The CO2 laser irradiation of the carbon target was carried out using the 9P(28) line at λ = 9.621 µm. This wavelength was checked with a 16-A spectrum analyser (Optical Eng. Co.). The pulse temporal profile is monitored with a photon drag detector (Rofin Sinar 7415). The temporal shape of the TEA-CO2 laser pulse consisted of a prominent spike of a full width at half maximum (FWHM) of 64 ns carrying ~90% of the laser energy, followed by a long lasting tail of lower energy and about 3 µs duration. The pulsed CO2 laser beam was perpendicularly focused with a NaCl lens of 24 cm focal length onto the target surface. The CO2 laser energy was measured in front of the lens with a Lumonics 20D pyroelectric detector through a Tektronix TDS 540 digital oscilloscope. The focused radius of the laser beam was measured at the target position with a pyroelectric array Delta Development Mark IV. The laser intensity (power density or irradiance) on the target surface ranges from 0.22 to 5.36 GW cm−2. The high purity graphite target (~99.99%) was placed in a low-vacuum cell equipped with a NaCl window for the laser beam and two quartz windows for optical access. The graphite target is initially at ambient temperature (298 K) and it is not water-cooled. The cell was evacuated with the aid of a rotary pump, to a base pressure of 4 Pa that was measured by a mechanical gauge. Optical emission from the plume was imaged by a collecting optical system onto the entrance slit of different monochromators. All the experimental measurements were taken at a constant distance of 1.5 cm from the target surface along the plasma expansion direction and 10 cm in the direction perpendicular to the plasma symmetry axis. In the low-resolution experiments the optical emission from the plume was collected and imaged onto an optical fibre using a quartz lens of 5 cm focal length. The quartz lens causes a slight chromatic aberration for OES measurements, although the geometric efficiency is barely affected. Two spectrometers were used: 1/8 m Oriel spectrometer (10 and 25 µm slits) with two different gratings (1200 and 2400 grooves mm−1) in the spectral region 2000–11000 Å at a resolution of ~1.3 Å
in first-order (1200 grooves mm\(^{-1}\) grating) and an ISA Jobin Yvon Spex (Model HR320) 0.32 m equipped with a plane holographic grating (2400 grooves mm\(^{-1}\)) in the spectral region 2000–7500 Å at a resolution of \(\sim 0.12 \, \text{Å}\) in first order. The detector is an Andor DU420-OE (open electrode) CCD (charge-coupled device) camera (1024 \times 256 matrix of 26 \times 26 \mu m\(^2\) individual pixels) with thermoelectric cooling working at \(-30^\circ\text{C}\). The low noise level of the CCD allows long integration times and therefore the detection of very low emission intensities. Many of the spectra were obtained with 5 s integration time over the entire luminous plasma event. The emission intensities. Many of the spectra were obtained with a 26 26 matrix of individual pixels) with thermoelectric cooling.

2. Laser parameters for the present experiments

The laser peak power or radiant pulse energy per time \(P_W\) (W) is given by

\[
P_W = E_W / \tau_{\text{FWHM}},
\]

\(E_W\) (J) being the pulse energy and \(\tau_{\text{FWHM}}\) (s) the pulse duration at the FWHM. The laser peak intensity (power density or irradiance) \(I_W\) (W cm\(^{-2}\)), fluence \(\Phi_W\) on target (J cm\(^{-2}\)), the photon flux \(F_{\text{ph}}\) (photon cm\(^{-2}\) s\(^{-1}\)) and electric field \(F_E\) (V cm\(^{-1}\)) are given by

\[
I_W = P_W / \pi r^2, \tag{2}
\]

\[
\Phi_W = E_W / \pi r^2, \tag{3}
\]

\[
F_{\text{ph}} = P_W \lambda / \pi r^2 c, \tag{4}
\]

\[
F_E = \sqrt{4} P_W / r^2 c, \tag{5}
\]

where \(\pi r^2\) is the focal spot area (cm\(^2\)) and \(\lambda\) is the laser wavelength. For the present experiments, the graphite ablation is performed using a high-power IR CO\(_2\) pulsed laser at \(\lambda = 9.621\, \mu\text{m}\), \(\tau_{\text{FWHM}} = 64\, \text{ns}\) and the focused-spot area was \(7.5 \times 10^{-3}\, \text{cm}^2\). For the different pulse laser energies measured in this work, the calculated laser peak power (equation (1)), intensity (equation (2)), fluence (equation (3)), photon flux (equation (4)) and electric field (equation (5)) are tabulated in table 1.

3. Results and discussion

3.1. Identification of the chemical species in the PLA plasma plume

In the scanned spectral region, from UV to NIR, OES reproduce particular emission of carbon plasmas in a low-vacuum air atmosphere \(P_{\text{atm}} = 4\, \text{Pa}\). Typical time-integrated and spectral-resolved low-resolution (1/8 m Oriel spectrometer to a resolution of \(\sim 1.3\, \text{Å}\) OES from PLA of graphite is shown in figures 2(a)–(f). In the recording of the spectra of figures 2(c)–(f) a cutoff filter was used in order to suppress high diffraction orders. These plasma plumes were generated by the CO\(_2\) laser intensity of 1.00 GW cm\(^{-2}\). In general, the spectra of the PLA plume are dominated by emission of strong electronic relaxation of excited atomic C, ionic fragments C\(^+\), C\(^{2+}\) and C\(^{3+}\) and molecular features of C\(_2\) (d \(3\Pi_g\)–\(\Delta\Pi_u\); triplet Swan band system). The medium-weak emission is mainly due to excited atomic N, H, O, ionic fragment C\(^{3+}\) and molecular features of C\(_2\) (E \(3\Sigma^+_g\)–\(\Delta\Pi_u\); Freymark system), C\(_2\) (D \(1\Sigma^+_g\)–\(\Pi^0_u\); Mulliken system), CN(D \(2\Pi\)–\(\Delta\Pi\); Phillips system), C\(_2\) (C \(1\Pi_u\)–\(\Sigma^+_g\); Deslandres–d’Azambuja system), OH(A \(2\Sigma^+\)–\(\Pi\)); CH(C \(2\Sigma^+\)–\(\Pi\)); NH(A \(3\Pi\)–\(X\)); CN(B \(2\Pi\)–\(X\)); C\(_2\) (e \(3\Pi_u\)–\(\Delta\Pi_u\); Phillips system) and CN(A \(3\Pi\)–\(X\)); red system).

In the spectrum of figure 2(a) in the 1920–3480 Å region, very strong atomic C, C\(^+\), C\(^{2+}\) and C\(^{3+}\) lines dominate, but also weak C\(^{3+}\) and molecular bands of C\(_2\) (E–A; \(\Delta v = v’ - v'' = +2, +1, 0\) sequence from 200 to 222 nm), C\(_2\) (D–X; \(\Delta v = 0\) sequence near 231.4 nm), CN(D–A; in the spectral range 223–260 nm), C\(_2\) (e–a; in the spectral range 240–290 nm), CN(B–X; \(\Delta v = 3\) sequence from 306 to 326 nm), OH(A–X; \(\Delta v = 0\) sequence from 306 to 318 nm), CH(C–X; \(\Delta v = 0\) sequence from 314 to 317 nm).
Figure 2. Low-resolution PLA of carbon emission spectrum observed in the 1920–9680 Å region at an air pressure of 4 Pa, excited by the 10µ(20) line at 944.20 cm⁻¹ of the CO₂ laser, and assignment of the atomic lines of C, C⁺, C²⁺, C³⁺, N, O and molecular bands of C₂(E ²Σ + A¹Π; Fremy system), C₂(D ²Σ – X¹Σ⁺; Mulliken system), C₂(e ¹Π → a¹Π; Fox–Herzberg system), CN(D²Π – A²Π), OH(A²Σ – X²Π), CH(C²Σ – X²Π), CN(B²Σ – X²Σ⁺; violet system), NH(A¹Π – X¹Σ⁻), C₂(C¹Π → A¹Π; Deslandres–d’Azambuja system), C₂(d ³Π → a¹Π; Swan band system), CH(B²Σ – X²Π), CH(A²Δ – X²Π), C₂(A¹Π → X¹Σ⁺; Phillips system) and CN(A²Π – X²Σ⁺; red system).
near 336 nm) and CN(B–X; Δν = 2 sequence from 326 to 348 nm) are observed. In this spectrum the predominant emitting species are the C2+ 2p2 1D2 → 2s2p 1P1 atomic line at 2296.87 Å, C 2p(3P3)3s 1P0 → 2p 1S1 atomic line at 2476.58 Å, two lines of C3+ at 2524.41 and 2529.98 Å, several lines of C (at 2836.71 and 2992.62 Å and the ν′ = 0 – ν″ = 0 band of NH(A–X) at 3360 Å. In the spectrum of figure 2(b), the predominant emitting species are C2+ (doublet 2s2s 2S1/2 → 2s3p 2P1/2,3/2) at 3918.98 and 3920.69 Å, respectively, and multiplet 2s34f 2F J → 2s3d 2D J′ around 4267 Å), and the molecular bands of CN(B–X; Δν = 0 sequence). Many medium intensity atomic lines of C+, C2+ and C3+, weak hydrogen lines of the Balmer series (Hα, Hβ, etc), and several molecular bands of CN, C2 and CH are also present. In the spectrum of figure 2(c), the predominant emitting species are C2+ and C2+ (molecular bands: e–a; Δν = 0, –1 and –2 sequences from 480 to 630 nm). Many weak lines of C, C+, C2+ and C3+ are also present. In the spectrum of figure 2(d), the most intense lines are the doublet structure of C2+ 2s3p 2P1/2,3/2 → 2s3d 2D1/2,3/2 at 6578.05 and 6582.88 Å, respectively, C2+ 2s2p 2P1/2 → 2s2p 2P1/2 at 6587.61 Å, C2+ 2s3d 2D1/2 → 2s3p 2P1/2 at 7231.32 Å and C2+ 2s3d 2D3/2 → 2s3p 2P3/2 at 7236.42 Å. Also many weak lines of C, C+, C2+, Hα, N, and several bands ν′–ν″ (5–1, 6–2, 7–3, 8–4, 3–0, 4–1, 5–2 and 6–3) corresponding to CN(A–X) are also present. The spectrum of figure 2(e) shows the emission of many atomic lines of C, O and N, the 3–0 band of C2(A–X) and several bands (2–0, 3–1, 4–2 and 5–3) of CN(A–X). Finally, in the spectrum of figure 2(f), the emission of many atomic lines of C and N and mainly the 1–0 and 2–1 bands of CN(A–X) can be appreciated.

For the assignment of the atomic lines of C, C+, C2+, C3+, C4+, H, N and O we used the information tabulated in NIST Atomic Spectral Database[34]. The observed emission molecular bands are identified using the spectroscopic information available in [35–39]. Moreover, these molecular bands were compared with the spectra obtained in our laboratory by conventional sources (free-burning carbon arc, propane–butane/air flame and acetylene/oxygen flame). As an example, figure 3 shows several time-resolved OES at low resolution from (a) PLA of carbon (air pressure of 4 Pa and CO2 laser power density $I_W = 1.00 \text{GW cm}^{-2}$); (b) acetylene/oxygen flame; (c) propane–butane/air flame; (d) free-burning carbon arc. In the acetylene/oxygen flame around 405 nm, several bands of the C3(A 1Π u–X 1Σg u) comet head group are observed which were not detected in the PLA of carbon. As shown in figure 3, ionic carbon lines C+, C2+, C3+ and C4+ cannot be observed in flames (figures 3(b) and (c)) or carbon electric arcs (figure 3(d)).

In order to get more insight into PLA of graphite and to obtain an unambiguous assignment of the emission lines and molecular bands, we have scanned the corresponding wavelength regions with higher resolution (~0.12 Å in first order). The spectra have been obtained with 24 successive exposures on the CCD camera in the spectral region 200–750 nm by a ISA Jobin Yvon Spex 0.32 m spectrometer. As examples, figures 4(a)–(f) show several spectra recorded in the PLA of carbon experiment at high resolution. These spectra were recorded under similar experimental conditions to low-resolution spectra (air pressure 4 Pa, CO2 laser excitation line 9P28 at 9.621 μm and laser intensity 5.36 GW cm$^{-2}$). The relative intensities of the observed emission lines reasonably agree with tabulated values in NIST Atomic Spectral Database[34]. In figures 4(a)–(f) we have indicated in italics the position of the band heads ν′–ν″ of the violet system of CN, and in regular typeface the bands of the other molecular systems. In figures 4(a)–(f), a rather complex structure is observed, in consequence of the overlapping between rotational lines of different molecular band systems. Figure 4(a) displays the overlapping between CH(C–X; Δν = 0 sequence), CN(B–X; Δν = 3 sequence) and OH(A–X; Δν = 0 sequence). The relative position of the main branches for the OH(A–X) 0–0 band is indicated. In figure 4(b), the high intensity of the 0–0 band for NH(A–X) is observed. This fact is in agreement with the high Franck–Condon factor (q00 = 0.9998) for this transition. In figure 4(c) a partial overlapping among CN(B–X; Δν = 1) and C2(C–A; Δν = 1) is observed. This spectrum clearly shows the reversal of the bands from ν′ = 5, which is due to the overlap between high vibrational quantum number bands with low vibrational quantum number bands. So, the first vibrational bands (1–0, 2–1, 3–2, 4–3 and 5–4) are shaded to the violet and after reversal (6–5, 7–6, . . . ) are shaded to the red. Figure 4(d) shows a portion of the rotational lines for the CH(B–X) 0–0 band with several single ionized carbon lines. A coincidence in the position among the CN(B–X) 4–4 and C2(C–A) 0–0 band heads is observed. In the spectrum of figure 4(e) the CN(B–X) Δν = –1 sequence, CH(A–X) 0–0 band and C2(a–d) Δν = 2 sequence were identified. Also, several C+, C2+, and atomic hydrogen lines are observed. Finally, figure 4(f) displays the rotational structure of the C2(d–a) 0–1, 1–2 and 2–3 bands. The spectral features clearly show
the complexity of the relaxation process and bring out the possibility of cascading processes.

### 3.2. Plasma excitation temperature measurements

The excitation temperature $T_{\text{exc}}$ was calculated according to the Boltzmann equation under the assumption of local thermodynamic equilibrium (LTE). In LTE plasmas, a single temperature characterizes all internal energy modes (electronic, vibrational and rotational). This temperature can be determined from the absolute intensity of any atomic or molecular feature or from Boltzmann plots of vibrational or rotational population distributions. The significance of this temperature depends on the degree of equilibrium within the plasma. For an optically thin plasma, the conditions satisfying this assumption of LTE require that the radiative population rates are negligible compared with the collisional population rates. This essentially implies that an excited state must have a higher probability of de-excitation by collision than by spontaneous emission. For plasma in LTE, any point can be
be described by its local values of temperature, density and chemical composition. Usually LTE is established among all the species in the plasma beyond \( \sim 1 \) μs delay time from the plasma start. For laser fluences around 10 J cm\(^{-2}\) the laser-induced plume, after \( \sim 1 \) μs, essentially contains only neutral atomic and molecular species, and electron density is expected to be very low. However, at higher laser fluences as used in this work (see table 1), in proximity to the carbon target surface, the plasma is formed by neutral atomic, highly ionized carbon and molecular species (see figures 2 and 4). The excitation temperature was calculated from the relative intensities of some C\(^+\) atomic lines (250–470 nm spectral region) from the slope of the Boltzmann plot \( \ln[I_{ki} \cdot \lambda_{ki} / g_k \cdot A_{ki}] \) versus \( E_k / k_B \) (figure 5):

\[
\ln \left[ \frac{I_{ki} \cdot \lambda_{ki}}{g_k \cdot A_{ki}} \right] = C_1 - \frac{E_k}{k_B \cdot T_{exc}} \tag{6}
\]

where \( I_{ki} \) is the emissivity (W m\(^{-1}\) sr\(^{-1}\)) of the emitted \( k \rightarrow i \) spectral line, \( \lambda_{ki} \) is the wavelength, \( g_k = 2J_k + 1 \) is the statistical weight, \( A_{ki} \) is the Einstein transition probability of spontaneous emission, \( E_k / k_B \) is the normalized energy of the upper electronic level (\( k_B \) is Boltzmann’s constant) and 

\[
C_1 = \ln(hcN_k/4\pi Q(T)) \quad \text{(}Q(T)\text{ is the partition function)}.
\]

The values of \( \lambda_{ki}, \; g_k, \; A_{ki}, \; E_k \) for C\(^+\) selected atomic lines were obtained from the NIST Atomic Spectral Database. The estimation of excitation temperature has been carried out from the PLA spectrum at a laser irradiance of 1.00 GW cm\(^{-2}\) (\( P_{\text{air}} = 4 \) Pa). The estimated excitation temperature was \( T_{\text{exc}} = 23000 \pm 1900 \) K (figure 5). These spectral lines were chosen based on their relative strengths, accuracies and transition probabilities. The relevant spectroscopic parameters for the C\(^+\) transitions have been listed in table 2.

### 3.3. Ionization degree of the plasma

As the CO\(_2\) laser beam is focused on the graphite surface, the carbon material absorbs the laser energy to melt, vaporize and excite the target material. The carbon vapour absorbs more energy and forms high temperature plasma near the surface. The plasma expands into the low-vacuum atmosphere (N\(_2\), O\(_2\), H\(_2\)O, etc) and transfers its energy to it. If the pressure around the target is greater than \( \sim 1000 \) Pa, the breakdown of the air takes place in a significant way. Neutral, single and highly ionized carbon emission lines are found close to the target graphite surface. The carbon clusters and the molecules of the atmosphere obtain an energy that exceeds the binding energy. In these conditions the plasma becomes a mixture of electrons, positive ions such as C\(^+\), C\(^{2+}\), C\(^{3+}\), C\(^{4+}\), neutral atoms such as C, N, O and H, and molecules such as C\(_2\), CN, CH, NH and OH in excited electronic states. In plasma there is a continuous transition from gases with neutral atoms to a state with ionized atoms, which is determined by an ionization equation. The transition between a gas and a plasma is essentially a chemical equilibrium, which shifts from the gas to the plasma side with increasing temperature. Let us consider the first three different ionization equilibria of carbon:

\[
C(2s^22p^2 3P_0) \leftrightarrow C^+ (2s^22p^2 2P_{3/2}), \quad + e + \text{IP(C-)}
\]

\[
C^+(2s^22p^2 2P_{3/2}) \leftrightarrow C^{2+} (2s^2 2S_0), \quad + e + \text{IP(C-II)}
\]

\[
C^{2+} (2s^2 2S_0) \leftrightarrow C^{3+} (2s^2 1S_0), \quad + e + \text{IP(C-III)}
\]

where the first three ionization potentials (IPs) for carbon are \( E_{\text{C-I}} = \text{IP(C-I)} = 11.2603 \) eV, \( E_{\text{C-II}} = \text{IP(C-II)} = 24.3833 \) eV and \( E_{\text{C-III}} = \text{IP(C-III)} = 47.8878 \) eV [40]. For each ionization equilibrium, the LTE between ionization and excitation was assumed.

### Table 2. List of C\(^+\) transition lines and their spectral database (NIST Atomic Spectra Database, 2006) used for plasma temperature calculation.

<table>
<thead>
<tr>
<th>Transition array</th>
<th>Air ( \lambda ) (Å)</th>
<th>( g_i )</th>
<th>( g_k )</th>
<th>( A_{ki} ) (s(^{-1}))</th>
<th>( E_i ) (cm(^{-1}))</th>
<th>( E_k ) (cm(^{-1}))</th>
<th>Rel. Int. (arb. uni.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>2059.12</td>
<td>2</td>
<td>4</td>
<td>4.53 \times 10(^7)</td>
<td>110 624.17</td>
<td>150 466.69</td>
<td>20 800</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>2512.06</td>
<td>4</td>
<td>6</td>
<td>5.42 \times 10(^7)</td>
<td>110 665.56</td>
<td>150 461.58</td>
<td>41 500</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>2746.49</td>
<td>2</td>
<td>4</td>
<td>4.36 \times 10(^7)</td>
<td>131 724.37</td>
<td>168 123.74</td>
<td>8500</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>2836.71</td>
<td>2</td>
<td>4</td>
<td>3.98 \times 10(^7)</td>
<td>96 493.74</td>
<td>131 735.52</td>
<td>76 900</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>2837.60</td>
<td>2</td>
<td>2</td>
<td>3.97 \times 10(^7)</td>
<td>96 493.74</td>
<td>131 724.37</td>
<td>44 700</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>3918.98</td>
<td>2</td>
<td>2</td>
<td>6.36 \times 10(^7)</td>
<td>131 724.37</td>
<td>157 234.07</td>
<td>7500</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>3920.69</td>
<td>4</td>
<td>2</td>
<td>1.27 \times 10(^8)</td>
<td>131 735.52</td>
<td>157 234.07</td>
<td>16 000</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>4267.00</td>
<td>4</td>
<td>6</td>
<td>2.23 \times 10(^9)</td>
<td>145 549.27</td>
<td>168 978.34</td>
<td>45 000</td>
</tr>
<tr>
<td>( 2s2p^2 2P_{3/2} \leftrightarrow 2s^22p^2 2P_{3/2} )</td>
<td>4267.26</td>
<td>6</td>
<td>8</td>
<td>2.38 \times 10(^9)</td>
<td>145 550.70</td>
<td>168 978.34</td>
<td>70 000</td>
</tr>
</tbody>
</table>

![Figure 5](image-url)
C\textsuperscript{2+} at a constant pressure of 4 Pa. The evolution of the laser-plasma can be divided into several transient phases. The initial plasma (\(\sim\))

The Saha equation (8) are 0.999, 0.999 and 0.28, respectively.

\(n_e \cdot N_i = \frac{g_e \cdot g_i (2 \pi m_e k_B T)^{3/2}}{\hbar^3} e^{-E_i/k_B T},\)

where \(n_e = N_i\) are the electron and ion densities in the different ionization equilibria, \(N_0\) the density of the carbon or ions in the first member of ionization equilibria, \(k_B\) Boltzmann’s constant, \(m_e\) the electron mass and \(g_e\) and \(g_i\) the statistical weights of the electrons (\(g_e = 2\)), C\textsuperscript{+} ions (\(g_i = 2\)), C\textsuperscript{2+} ions (\(g_i = 2\) and C neutrals (\(g_i = 1\)). The Saha equation reads

\(\frac{n_e \cdot N_i}{N_0} = CT^{3/2} e^{-E_i/k_B T},\)

with \(C = 9.6587 \times 10^{31}, 2.4147 \times 10^{31}\) and \(9.6587 \times 10^{21}\) K\textsuperscript{-2/3} m\textsuperscript{-3} for the first three ionization equilibria of carbon, respectively, and \(T\) is in K. Figure 6 shows the ionization degree \(N_i/(N_0 + N_i)\) of C, C\textsuperscript{+} and C\textsuperscript{2+}, plotted as a function of the gas temperature \(T\) at a constant total pressure \(P = (N_0 + n_e + N_i) k_B T\) of 4 Pa. The graph shows that carbon is already fully ionized at thermal energies well below the first ionization energy of 11.2603 eV (equivalent to 130\,670 K). If we consider a temperature of 23\,000 K, the ionization degrees of C, C\textsuperscript{+} and C\textsuperscript{2+} obtained by means of the Saha equation (8) are 0.999, 0.999 and 0.28, respectively. These so high values of the ionization degrees justify the observed emission spectra. Keeping in mind these results, the temperature obtained from the relative intensity of C\textsuperscript{+} lines was chosen as the first approximation for the excitation temperature.

3.4. Electron number density

The evolution of the laser-plasma can be divided into several transient phases. The initial plasma (\(\sim\))

is characterized by high electron and ion densities (10\textsuperscript{17}–10\textsuperscript{20} cm\textsuperscript{-3}) and temperatures around 30\,000 K. Of course, the density gradient of the plasma is highest in the earliest time of plume expansion. The emission spectrum for the early stage of the plasma is characterized by a continuum background emission mainly due to bremsstrahlung and recombination processes of electrons with ions in the plasma. Structured emission spectra from atomic and ionized species and molecular bands can be found after about 300 ns delay. Observed spectral lines are always broadened, partly due to the finite resolution of the spectrometer and partly to intrinsic physical causes. The principal physical causes of spectral line broadening are the Doppler, resonance pressure and Stark broadening. The Doppler broadening is due to the thermal motion of the emitting atoms or ions. For a Maxwellian velocity distribution the line shape is Gaussian, and the FWHM may be estimated as (Å):

\[\Delta \lambda_{\text{FWHM}} = 7.16 \times 10^{-7} \cdot \lambda \cdot \sqrt{T/M},\]

\(\lambda\) being the wavelength in Å, \(T\) the temperature of the emitters in K, and \(M\) the atomic mass in amu. In our experiments, for C\textsuperscript{+} lines, the Doppler line widths are 0.08–0.13 Å at 23\,000 K. Stark line broadening from collisions of charged species is the primary mechanism influencing the emission spectra in these experiments. The FWHM of the Stark broadened lines is related to the electron number density \(n_e\) (cm\textsuperscript{-3}) by [41]

\[\Delta \lambda_{\text{FWHM}}^2 = 2W \left(\frac{n_e}{10^{16}}\right) + 3.5A \left(\frac{n_e}{10^{16}}\right)^{1/4} \times \left(1 - BN_D^{-1/3}\right) W \left(\frac{n_e}{10^{16}}\right),\]

where \(W\) is the electron impact parameter or half-width, \(A\) is the ion impact parameter, both in Å, \(B\) is a coefficient equal to 1.2 or 0.75 for ionic or neutral lines, respectively, and \(N_D\) is the number of particles in the Debye sphere

\[N_D = 1.72 \times 10^6 \frac{T^{3/2}}{n_e^{1/2}}.\]
The electron and the ion impact parameters are functions of temperature. The first term on the right side of equation (9) refers to the broadening due to the electron contribution, whereas the second one is the ion broadening. Since for PLA conditions Stark broadening is predominantly by electron impact, the ion correction factor can safely be neglected, and equation (9) becomes

$$\Delta \lambda_{\text{FWHM}} = 2W\left(\frac{n_e}{10^{16}}\right).$$

(11)

The choice of plasma emission for $n_e$ measurements is made to ensure that the C+ spectral lines are sensitive enough to the Stark effect and do not suffer from interference by other species. In our case, the estimation of electron density $n_e$ has been carried out by measuring the broadening of the spectral profiles of isolated lines of C+ (2174, 2747, 2837, 2993, 3877, 3920, 4267 and 5890 Å) from the high-resolution spectra. The electron number densities of the laser-induced plasma were determined at a laser power density of $W_L = 1$ GW cm$^{-2}$ and air pressure of 4 Pa. A Lorentz function was used to fit the spectra. In order to extract the Stark broadening from the total experimentally measured line broadening, we have to previously deconvolute the different effects that contribute to the broadening of the spectral line: the instrumental, Doppler and Stark broadenings. Values of the electron impact half-width $W$ were taken from the extensive tables given by Griem [41]. Determination of electron density $n_e$ by this method is independent of any assumptions regarding LTE conditions. Electron densities in the range $(0.69-5.6) \times 10^{16}$ cm$^{-3}$, with an estimated uncertainty of 10%, were determined from the Stark broadening data of several singly ionized carbon lines. The validity criteria for LTE and consequently criteria for the application of the different spectroscopic methods are extensively discussed in the literature [42,43]. For the LTE, the excited states have to be populated through collisions. Using the McWhirter’s criterion [44] to check the condition for the validity of the LTE, we find that the electron number density satisfies

$$n_e \geq 1.6 \times 10^{12} T^{1/2} (\Delta E)^3.$$  

(12)

Here, $n_e$ (cm$^{-3}$) is the electron density, $T$ (K) is the plasma temperature and $\Delta E$ (eV) is the difference in the energies between the upper and the lower states of all the C+ investigated transitions. At the evaluated temperature of 23 000 ± 1900 K, equation (12) yields $n_e \approx (0.39-2.2) \times 10^{16}$ cm$^{-3}$. These electron densities are close to the measured values. Based on these calculations, it is difficult to tell whether the plasma is in LTE or not. A possible reason for non-thermal equilibrium could be the large integration time used in the experiments. At these later times, the collisions among the species decrease due to drop in densities.

3.5. Effect of laser irradiance

Laser–sample and laser–plasma interactions are strongly dependent on the laser beam irradiance on the target. To see the effect of laser irradiance the measurements were also carried out at different laser fluences. Optical emission spectra of the carbon plasma plume in low vacuum (~4 Pa) as a function of the laser intensity are shown in figures 7(a) and (b). As indicated above, these spectra were recorded at a constant distance of 1.5 cm from the target surface along the plasma expansion direction and after the incidence of only one pulse of the CO2 laser. The data were measured at a delay of 20 ms. As we have already indicated above, the laser pulse consisted of a 64 ns spike carrying ~90% of the energy and a 3 μs lasting tail. For example, for a laser pulse energy of 2685 mJ, the laser power or radiant pulse energy per time (equation (1)) of the spike is 37.7 and 0.089 MW for the tail. Considering the fast plume expansion, the major part of the tail of the laser pulse will reach the target. Using this laser pulse one can expect that the leading edge of the 64 ns pulse will create plasma above the target and the 3 μs lasting tail will be used for heating the plasma, without producing further ablation. An increase in atomic and molecular emission intensity with increasing laser fluence was observed. Figure 8 shows the emission intensity change of C(247.856 nm), C$^+$ (251.206 nm), C$^{2+}$ (269.775 nm), C$^{3+}$ (252.998 nm), C$^{4+}$ (227.792 nm), OH 0–0 band head (306.35 nm) and NH 1–0 band head (336.00 nm) as a function of the carbon dioxide laser fluence. The C$^{3+}$, C$^+$ and C emission intensity increases drastically with the laser fluence. Beyond ~100 J cm$^{-2}$, a sharp increase in atomic...
were analysed in order to calculate the molecular vibrational laser fluence.

At higher laser fluences (154–342 J cm

The emission characteristics of the laser-induced plasma are influenced to a large extent by the nature and composition of the surrounding atmosphere. The pressure of the air ambient atmosphere is one of the controlling parameters of the plasma characteristics, as well as the factors related to the laser energy absorption. The presence of air during the ablation process has dramatic consequences on the expansion dynamics. An interesting observation was the effect of the air pressure,
studied in the range 4.6–63 500 Pa. Figures 12 and 13 show typical OES from a carbon plasma plume at different air pressures. These plasma plumes were generated by the CO2 laser intensity of 1.00 GW cm−2. In general, the spectra of the PLA plume at low pressures (P < 1500 Pa) are dominated by emission of electronic relaxation of excited atomic C, N, H, O, ionic fragments C+, C2+, C3+ and C4+, and molecular features of C2(E–A), C2(D–X), C2(d–a), C2(D–X), C2(e–a), C2(C–A), C2(A–X), CN(D–A), CN(B–X), CN(A–X), OH(A–X), NH(A–X), CH(C–X), CH(B–X) and CH(A–X). The spectra of the PLA plume at high pressures (P > 10 000 Pa) are dominated by emission of electronic relaxation of excited atomic N, O, H, ionic fragments N2+ and O2+, and molecular features of CN(B–X) and CN(A–X). The intensities of the C2 1–0 band head of the C1Π2−A1Π1 (3607 Å), C2 1–0 band head of the D1Σu+−X1Σg (4737 Å), CN 1–0 and 0–0 band heads of the B2Σg+−X2Σg violet system, CH 0–0 band head of the A2Δ−X2Π (4307 Å), N2+(3437 Å), O(3410 Å), C2+(3919 Å), C2+(4267 Å), C2+(4593 Å), C3+(4657 Å) and H2 atomic lines as a function of air pressure. From figure 14, the intensity of the C2+ (4593 Å), C2+ (4267 Å) and C3+ (4657 Å) spectral lines increase with increasing pressure, reach a maximum at about 200 Pa, and then decrease with higher pressures. Similar results were reported in the literature [45, 46]. Figure 14 shows the evolution of the emission intensity of the C2 1–0 band head of the C1Π2−A1Π1 (3607 Å), C2 1–0 band head of the D1Σu+−X1Σg (4737 Å), CN 1–0 and 0–0 band heads of the B2Σg+−X2Σg violet system, CH 0–0 band head of the A2Δ−X2Π (4307 Å), N2+(3437 Å), O(3410 Å), C2+(3919 Å), C2+(4267 Å), C2+(4593 Å), C3+(4657 Å) and H2 atomic lines as a function of air pressure. From figure 14, the intensity of the C2+ (4593 Å), C2+ (4267 Å) and C3+ (4657 Å) spectral lines increase with increasing pressure, reach a maximum at about 200 Pa, and then decrease with higher pressures. Similar results were reported in the literature [45, 46]. Figure 14 shows the evolution of the emission intensity of the C2 1–0 band head of the C1Π2−A1Π1 (3607 Å), C2 1–0 band head of the D1Σu+−X1Σg (4737 Å), CN 1–0 and 0–0 band heads of the B2Σg+−X2Σg violet system, CH 0–0 band head of the A2Δ−X2Π (4307 Å), N2+(3437 Å), O(3410 Å), C2+(3919 Å), C2+(4267 Å), C2+(4593 Å), C3+(4657 Å) and H2 atomic lines as a function of air pressure. From figure 14, the intensity of the C2+ (4593 Å), C2+ (4267 Å) and C3+ (4657 Å) spectral lines increase with increasing pressure, reach a maximum at about 200 Pa, and then decrease with higher pressures. Similar results were reported in the literature [45, 46].
target than the N\(^+\) and O\(^+\) emissions produced nearer to the air plasma position. In general, the ambient gas will confine the plasma near the target (produced mainly by C, C\(^+\), C\(^{2+}\), C\(^{3+}\) and CN, C\(_{2}\), CH) and prevent the electrons and species produced near the target from escaping quickly from the laser focal volume (observation region). Therefore, the emission intensity increases with increasing pressure. However, at higher pressures (more than 200 Pa in our case), the ambient gas will hinder the plasma from penetrating the atmosphere and predictably cause a higher plasma temperature. The emission intensity of H, C, C\(^{+}\), C\(^{2+}\), C\(^{3+}\) and CN, C\(_{2}\), CH decreases because of the fact that the laser energy is absorbed by air, producing air breakdown and increasing the N, O, N\(^+\) and O\(^+\) emission intensity, in agreement with our observation in figure 13. At lower air pressures, the absence of the shielding air plasma results in a strong increase in the intensity of the C, C\(^{+}\), C\(^{2+}\), C\(^{3+}\) emission from the carbon target plasma. At such lower air pressures the relative contribution of the N\(^+\), O and O\(^+\) emission diminishes, and the emission from the carbon surface component becomes dominant.

4. Conclusions

The PLA generated by CO\(_{2}\) laser pulses in graphite in a low-vacuum atmosphere has been investigated by means of OES. The emission observed in the plasma region is mainly due to the relaxation of excited atomic C, N, O and H, ionic fragments C\(^{+}\), C\(^{2+}\), C\(^{3+}\), and C\(^{+}\), and molecular bands of C\(_{2}\)(E–A), C\(_{2}\)(d–a), CN(D–A), CN(B–X), CN(A–X), C\(_{2}\)(D–X), C\(_{2}\)(e–a), C\(_{2}\)(C–A), OH(A–X), NH(A–X), CH(C–X), CH(B–X) and CH(A–X). An excitation temperature around 23 000 K and electron densities in the range (0.6–5.6) \(\times\) 10\(^{16}\) cm\(^{-3}\) were estimated by means of C\(^{+}\) lines. Estimates of vibrational temperatures of C\(_{2}\) electronically excited species under various laser power density conditions are made. The characteristics of the spectral emission intensities from different species have been investigated as functions of the ambient pressure and laser irradiance.

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