Optical emission spectroscopy of oxygen plasma induced by IR CO₂ pulsed laser

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys. D: Appl. Phys. 41 215206

(<http://iopscience.iop.org/0022-3727/41/21/215206>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 161.111.22.141

The article was downloaded on 13/12/2012 at 08:54

Please note that [terms and conditions apply](#).

Optical emission spectroscopy of oxygen plasma induced by IR CO₂ pulsed laser

J J Camacho¹, M Santos², L Díaz² and J M L Poyato¹

¹ Departamento de Química-Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain

² Instituto de Estructura de la Materia, CFMAC, CSIC, Serrano 121, 28006-Madrid, Spain

E-mail: j.j.camacho@uam.es

Received 4 July 2008, in final form 1 September 2008

Published 14 October 2008

Online at stacks.iop.org/JPhysD/41/215206

Abstract

Laser-induced breakdown (LIB) spectroscopy in oxygen at room temperature and pressures ranging from 4.6 to 75 kPa was studied using a high-power transverse excitation atmospheric CO₂ laser ($\lambda = 9.621$ and $10.591 \mu\text{m}$; $\tau_{\text{FWHM}} = 64$ ns; power densities ranging from 0.87 to 6.31 GW cm^{-2}). The spectrum of the generated plasma is dominated by emission of strong O, O⁺ and weak O²⁺ atomic lines. Excitation temperatures of $31\,500 \pm 1600$ K and $23\,000 \pm 3000$ K were estimated by means of O²⁺ and O⁺ ionic lines, respectively. Electron number densities of the order of $(3.5\text{--}16.5) \times 10^{16} \text{ cm}^{-3}$ were deduced from the Stark broadening of several ionic O⁺ lines. The characteristics of the spectral emission intensities from different species have been investigated as functions of the oxygen pressure and laser irradiance. Optical breakdown threshold intensities in O₂ at $10.591 \mu\text{m}$ have been determined. The physical processes leading to LIB of oxygen have been analysed.

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

1. Introduction

Oxygen, being the third most abundant element in the universe by mass [1], one of the most abundant constituents in the Earth's atmosphere and the most abundant element by mass in the Earth's crust, is of great interest to many different researchers. It is well known that gases such as O₂ under normal absorption conditions are relatively transparent to laser radiation. However, when the laser intensity increases and reaches a certain threshold value they are no longer transparent. The laser-induced breakdown (LIB) is characterized by an intense plasma or spark, brilliant flash and a cracking noise. Measurements of the emission spectra revealed a highly ionized plasma which expanded somewhat like a blast wave into the surrounding medium. Since the first observations of LIB in gases [2], the phenomenon has been studied extensively, both theoretically and experimentally [3–11]. Among the various diagnostic techniques which are convenient tools for detecting various transient species from UV up to IR spectral regions, optical emission spectroscopy (OES) has definite advantages pertaining to high spatial and temporal resolution without perturbation of the laser-induced plasma.

Laser-induced breakdown spectroscopy (LIBS) is a simple spectrochemical technique in which a laser beam is directed at a sample to create a high-temperature plasma. Several reviews on the LIBS principle and applications can be found in [12–18]. Detailed studies of LIBS on N₂, Si₃H₈ and graphite have been recently made in our laboratory [19–21]. Though many breakdown measurements have been carried out in air and nitrogen, there is much less data on oxygen. Several laser-induced breakdown threshold measurements have been carried out in oxygen [22–27]. However, very limited data are available on the laser-induced plasma emission spectrum in oxygen [24, 28]. The LIBS oxygen spectrum recorded by Nordstrom [28] in the spectral region 350–950 nm is composed of O and O⁺ atomic lines.

In this work, LIB generated by CO₂ laser pulses in O₂ has been investigated by means of OES. The plasma induced in oxygen with pressures ranging from 4.6 to 75 kPa has been measured and analysed. Optical breakdown threshold intensities in oxygen at $10.591 \mu\text{m}$ have been measured. The strong emission observed in the plasma region is mainly due to the relaxation of excited atomic O and ionic fragments O⁺ and O²⁺. Excitation temperatures and electron densities were

calculated by means of different O^{2+} and O^+ ionic lines. The physical processes leading to LIB of oxygen in the power density range from 0.87 to 6.31 $GW\ cm^{-2}$ have been analysed.

2. Experimental

2.1. Experimental details

The LIBS system has been described in earlier publications [19–21], hence only a brief overview of the system will be presented. The laser-induced plasma was generated using a transverse excitation atmospheric (TEA) CO_2 laser (Lumonics model K-103) operating on an 8 : 8 : 84 mixture of CO_2 : N_2 : He, respectively. 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 CO_2 laser irradiation of the gas was carried out using the 9P(28) line at $\lambda = 9.621\ \mu m$ ($\Delta E = 0.1289\ eV$) and the 10P(20) line at $\lambda = 10.591\ \mu m$ ($\Delta E = 0.1171\ eV$). These wavelengths were checked with a 16 A spectrum analyser (Optical Eng. Co.). The pulse temporal profile was monitored with a photon drag detector (Rofin Sinar 7415). The temporal shape of the TEA- CO_2 laser pulse consisted of a prominent spike of full width at half maximum (FWHM) of 64 ns carrying $\sim 90\%$ of the laser energy, followed by a long lasting tail of lower energy and about 3 μs duration. The laser pulse repetition rate is usually 1 Hz. The divergence of the emitted laser beam is 3 mrad. The pulsed CO_2 laser beam was focused with a NaCl lens of 24 cm focal length onto the centre of the gas cell. The primary laser beam was angularly defined and attenuated by two diaphragms of 25 and 17.5 mm diameter before entering the gas cell. The CO_2 laser averaged energy was measured in front of the lens with a Lumonics 20D pyroelectric detector through a Tektronix TDS 540 digital oscilloscope. Brewster losses were determined by making pulse energy measurements with and without the NaCl window in place. The focused radius of the laser beam (0.499 mm) was measured at the target position with a pyroelectric array Delta Development Mark IV. The laser intensity (power density or irradiance) on the focal volume ranged from 0.86 to 6.31 $GW\ cm^{-2}$. The laser power density energy was varied using several calibrated CaF_2 attenuators. Experimental threshold power densities for oxygen were measured for the TEA- CO_2 laser at $\lambda = 10.591\ \mu m$. The threshold power densities for oxygen at a given pressure were measured in the following two manners. First 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 and then it was filled with oxygen up to the desired pressure. The TEA- CO_2 laser was fired and its energy transmitted through the cell was increased until breakdown was observed in 50% of laser pulses. The threshold was easily determined because it was always associated with the appearance of a blue bright flash of light in the focal region, with a cracking noise, and the abrupt absorption of the laser pulse transmitted through the focal region. Another way to measure the threshold was to induce a previous breakdown at a pressure over the desired value, later the pressure was lowered and the energy adjusted until the breakdown began with some probability, usually around 50%. This method

is similar to inducing the breakdown with energy in excess and to attenuating the laser until the spark disappears. The present experiments showed that when high laser energy was used, oxygen breakdown occurred easily and it was reproducible. When the laser energy was reduced to its threshold power density value, oxygen breakdown became a sporadic event. Such sporadic behaviour might be due to the difficulty in generating seed electrons at the breakdown threshold values. The primary O_2 studied in these experiments was of research grade purity ($>99.995\%$). Oxygen gas, initially at ambient temperature (298 K), was placed in a cell equipped with a NaCl window for the laser beam input and two quartz windows for optical access. Optical emission from the plasma plume was collected onto the entrance slit of different monochromators. All the experimental measurements were taken at the focal point at 10 cm in the direction perpendicular to the plasma symmetry axis. Two spectrometers were used: a 1/8 m Oriel spectrometer (25 μm slit and grating of 1200 grooves mm^{-1}) in the spectral region 2000–10 500 $\text{\AA}$ at a resolution of $\sim 1.3\ \text{\AA}$ in first order with an Andor DU420-OE (open electrode) CCD camera (1024 $\times$ 256 matrix of 26 $\times$ 26 μm^2 individual pixels) with thermoelectric cooling working at $-30\ ^\circ C$ and a 0.32 m ISA Jobin Yvon Spex (Model HR320) spectrometer (adjustable slit and holographic grating of 2400 grooves mm^{-1}) in the spectral region 1900–7500 $\text{\AA}$ at a resolution of $\sim 0.10\ \text{\AA}$ in first order with an Andor iStar DH734 ICCD camera (1024 $\times$ 1024 matrix of 25 $\times$ 25 μm^2 individual pixels) with thermoelectric cooling working at $-20\ ^\circ C$. The low noise level of the ICCD 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 intensity response of the detection system was calibrated with a standard (Osram No. 6438, 6.6 A, 200 W) halogen lamp and an Hg/Ar pencil lamp. Several (Cu/Ne, Fe/Ne and Cr/Ar) hollow cathode lamps (HCLs) were used for the spectral wavelength calibration of the spectrometers.

2.2. Laser parameters for the present experiments

Since different authors characterize the laser field values in different ways, we give here the relationships between the laser peak power, the peak intensity, the fluence, the photon flux density and the electric field. The laser peak power or radiant pulse energy per time P_W (in W) is given by

$$P_W = E_W / \tau_{FWHM}, \quad (1)$$

where E_W (in J) is the pulse energy and τ_{FWHM} (in s) is the pulse duration at the FWHM. The laser peak intensity (power density or irradiance) I_W ($W\ cm^{-2}$), fluence Φ_W on the focused-spot area ($J\ cm^{-2}$), the photon flux F_{ph} (photon $cm^{-2}\ s^{-1}$) and electric field F_E ($V\ cm^{-1}$) are given by

$$I_W = P_W / \pi r^2, \quad (2)$$

$$\Phi_W = E_W / \pi r^2, \quad (3)$$

$$F_{ph} = I_W \lambda / hc, \quad (4)$$

$$F_E = \sqrt{I_W / c \epsilon_0}, \quad (5)$$

Table 1. Laser parameters for the present experiments.

Laser wavelength (μm)	Energy E_W (mJ)	Power P_W (MW)	Intensity I_W (GW cm^{-2})	Fluence Φ_W (J cm^{-2})	Photon flux F_{ph} ($\text{ph. cm}^{-2} \text{s}^{-1}$)	Electric field F_E (MV cm^{-1})
9.621	2685	42.1	5.36	342	2.60×10^{29}	1.50
9.621	2256	35.4	4.50	287	2.18×10^{29}	1.37
9.621	1732	27.1	3.46	220	1.67×10^{29}	1.20
9.621	1209	19.0	2.41	154	1.17×10^{29}	1.01
9.621	503	7.88	1.00	64.0	4.86×10^{28}	0.65
10.591	3161	49.5	6.31	402	3.36×10^{29}	1.63
10.591	2145	33.6	4.28	273	2.28×10^{29}	1.34
10.591	1481	23.2	2.96	189	1.58×10^{29}	1.11
10.591	968	15.2	1.93	123	1.03×10^{29}	0.90
10.591	624	9.78	1.25	79.5	6.64×10^{28}	0.72
10.591	436	6.83	0.87	55.5	4.64×10^{28}	0.60

Figure 1. Laser-induced breakdown produced in oxygen at 49.0 kPa by a TEA-CO₂ laser pulse ($\lambda = 10.591 \mu\text{m}$ and power density of 1.93 GW cm^{-2}). Laser beam direction is from right to left.

where πr^2 is the focal spot area (cm^2), λ is the laser wavelength, h is the Planck constant, c is the speed of light and ϵ_0 is the electric constant. The laser intensity, fluence, photon flux and electric field at the focal volume are inversely proportional to the focused spot size. For the present experiments, the LIB on oxygen is performed using a high-power IR CO₂ pulsed laser at $\lambda = 9.621$ and $\lambda = 10.591 \mu\text{m}$, $\tau_{\text{FWHM}} = 64 \text{ ns}$, and the measured focused-spot area was $7.85 \times 10^{-3} \text{ cm}^2$. 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 given in table 1.

3. Results and discussion

3.1. Plasma visualization

When a sample of oxygen is irradiated by CO₂ laser lines of sufficient power, a visible bluish bright flash occurs. Figure 1 shows an example of an LIB plasma in oxygen induced by a single CO₂ laser pulse. The cell was initially filled at room temperature with O₂ at 49.0 kPa. The laser was focused on a

point at the centre of the cell. A number of plasma lobes can be distinguished as well as diffuse, luminous cloud surrounding the central plasma core. The observations of the LIB geometry during the experiments indicate that the actual plasma region is not entirely spherical, but slightly elongated in the direction of the laser beam propagation.

3.2. Identification of the chemical species in the laser-induced oxygen plasma

To understand the detailed aspects of laser-beam interaction with the gas and recombination processes following the breakdown, time-resolved studies of the emission spectra from the plasma offer the most convenient approach. The emission spectrum has a continuum on which the emission lines are superimposed. This continuum extends over the whole range of wavelength and has been subtracted in our spectra.

Figures 2(a)–(f) display an overview of the low-resolution LIB emission spectrum (2320–9690 Å) in oxygen at a pressure of 53.2 kPa, excited by the 10P(20) line of the CO₂ laser, and assignment of the atomic lines of O, O⁺, O²⁺, N and N⁺ [29]. Strong atomic O lines dominate the spectrum but ionic O⁺ lines (about 8 times weaker) and weak O²⁺ lines (about

Figure 2. (a)–(f) Low-resolution LIB emission spectrum observed in the 2320–9690 Å region in oxygen at a pressure of 53.2 kPa, excited by the 10P(20) line of the TEA-CO₂ laser at 10.591 μm and a power density of 0.87 GW cm⁻², and assignment of the atomic lines of O, O⁺, O²⁺, N and N⁺.

150 times weaker) are also present. Atomic and ionic nitrogen lines were present, as well as the first negative band system 330–400 nm corresponding to the transition $B^2\Sigma_u^+-X^2\Sigma_g^+$ in N_2^+ . In the acquisition of the spectrum of figures 2(d)–(f) a cut-off filter was used to suppress the second order intense UV oxygen atomic lines. This cut-off filter produces a decrease in the intensity with regard to the spectra of figures 2(a)–(c). In order to get more insight into LIB of oxygen and to obtain an unambiguous assignment of the emission lines, we have scanned the corresponding wavelength regions with a higher resolution (~ 0.10 Å in first-order), which was sufficient to distinguish clearly between nearly all observed lines. The spectra have been obtained with fifty successive exposures on the ICCD camera in the spectral region 1900–7500 Å. As examples, figures 3(a)–(f) show several spectra recorded in the LIB experiment. These LIB emission spectra were recorded under the following experimental conditions: oxygen pressure of 48.8 kPa, excitation line 10P(20) at 10.591 μm and CO_2 laser power density 4.28 GW cm^{-2} . Figures 3(a)–(f) display some details of the large features found in figures 2(a)–(f). No new features were observed in these high-resolution spectra. In these figures, multiplet transitions between different J levels for O^+ and O^{2+} are observed. In some cases these multiplet structures are not completely resolved due to Stark broadening of atomic lines. The relative intensities of the observed emission lines reasonably agree with the tabulated values in the NIST Atomic Spectral Database [29]. The spectral features clearly show the complexity of the relaxation process and bring out the possibility of cascading processes.

3.3. Plasma excitation temperature measurement

We have calculated the excitation temperature T_{exc} according to the Boltzmann equation under the assumption of local thermodynamic equilibrium (LTE). The conditions satisfying this assumption of LTE require that the radiative depopulation rates are negligible compared with the collisional depopulation rates. This essentially implies that an excited state must have a higher probability of de-excitation by collision than by spontaneous emission. Generally LTE is established among all the species in the plasma beyond ~ 1 μs delay time from the plasma start.

The excitation temperature was calculated from the relative intensities of several O^+ (3270–3310 Å spectral region) and O^{2+} (2900–3350 Å spectral region) atomic lines and the slope of the Boltzmann plot $\ln[I_{ki} \cdot \lambda_{ki} / g_k \cdot A_{ki}]$ versus E_k / k_B :

$$\ln \left[\frac{I_{ki} \cdot \lambda_{ki}}{g_k \cdot A_{ki}} \right] = C - \frac{E_k}{k_B \cdot T_{\text{exc}}}, \quad (6)$$

where I_{ki} is the emissivity in $\text{W m}^{-3} \text{sr}^{-1}$ of the emitted $k \rightarrow i$ spectral line, λ_{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 and $C = \ln(hcN_k / 4\pi Q(T))$ ($Q(T)$ is the partition function). The values of λ_{ki} , g_k , A_{ki} and E_k for O^+ and O^{2+} selected atomic lines were obtained from the NIST Atomic Spectral Database [29]. The excitation temperatures were determined under the following experimental conditions:

oxygen pressure of 48.8 kPa, excitation line 10P(20) at 10.591 μm and CO_2 laser power density 4.28 GW cm^{-2} . The obtained excitation temperatures, in the case of O^+ and O^{2+} , were $23\,000 \pm 3000$ K and $31\,500 \pm 1600$ K, respectively (figure 4). This behaviour can be due to the different quenching rate coefficients between each species. Also this fact may be interpreted to result from the different emissivity distributions of single ionized and double ionized oxygen lines. The emissivity of the double ionized lines is produced, on average, near the laser-induced plasma inner region with higher temperature. In contrast, the emissivity of the single ionized lines comes, on average, from the low-temperature region close to the plasma front, where the double ionized atom density is lower. The intensity measurements correspond to the integration of the local emissivity values along the line of sight, integrated in turn in the perpendicular directions. As a consequence, the single ionized oxygen Boltzmann plot provides a temperature value which is a certain average of the low-temperature values in the plasma (23 000 K), whereas the temperature obtained from the double ionized Boltzmann plot (31 500 K) averages the values existing in the high-temperature region. Keeping in mind these results, the temperature obtained from the relative intensity of O^+ atomic lines (23 000 K) was chosen as the first approximation for the excitation temperature. Real plasmas provide, even in the worst cases, just an approximation to LTE. However, their spatial inhomogeneity is very large as concerns the temperature and number density distributions of the different species. Consequently, the LTE occurs only within a very small volume of the plasma.

3.4. Ionization degree of the plasma

When dielectric breakdown is produced in oxygen under high intensity laser radiation, some molecules can obtain an energy that exceeds the binding energy. Also some of their electrons become so energetic that the atoms and molecules ionize. Taking into account our experimental spectral observations, at these high temperatures oxygen becomes a mixture mainly of primary O_2 , O , O^+ , O^{2+} and electrons. The transition between a gas and plasma is essentially a chemical equilibrium which shifts from the gas to the plasma side with increasing temperature. Let us consider the first two different ionization equilibria of oxygen:

where the first two ionization potentials (IPs) for oxygen are $I_P(\text{O} - \text{I}) = 13.618$ eV and $I_P(\text{O} - \text{II}) = 35.121$ eV [30]. For each ionization equilibrium, the LTE between ionization and recombination reactions at temperature T is described by the Saha equation

$$\frac{n_e \cdot N_i}{N_0} = \frac{g_e \cdot g_i}{g_0} \frac{(2\pi m_e k_B T)^{3/2}}{h^3} e^{-I_P / k_B T}, \quad (7)$$

where $n_e = N_i$ are the electron and ion densities in different ionization equilibria in the second member of ionization

Figure 3. (a)–(f) High-resolution LIB emission spectrum observed in several spectral regions in oxygen at a pressure of 48.8 kPa, excited by the CO₂ laser at 10P(20) line (10.591 μ m) with a power density of 4.28 GW cm⁻², and assignment of some atomic lines of O⁺, O²⁺, and N⁺.

Figure 4. Linear Boltzmann plots for several O^+ and O^{2+} transition lines used to calculate plasma temperature, T_{exc} . Plots also show a linear fit to the data.

Figure 5. Temperature dependence of the ionization degree $N_i/(N_0 + N_i)$ of atomic oxygen O and oxygen singly ionized O^+ at a constant pressure of 53.2 kPa.

equilibria, N_0 the density of the oxygen or ions in the first member of ionization equilibria, h is Planck's constant, k_B is Boltzmann's constant, m_e the electron mass and g_e , g_i and g_0 the statistical weights of the electrons ($g_e = 2$), O^+ ions ($g_i = 4$), O^{2+} ions ($g_i = 1$) and O neutrals ($g_0 = 5$). The Saha equation reads

$$\frac{n_e \cdot N_i}{N_0} = C T^{3/2} e^{-I_p/k_B T}, \quad (8)$$

where $C = 3.864 \times 10^{21} \text{ K}^{-2/3} \text{ m}^{-3}$ and $1.207 \times 10^{21} \text{ K}^{-2/3} \text{ m}^{-3}$ for the first two ionization equilibria of oxygen, respectively, and T is in K. Figure 5 shows the ionization degree $N_i/(N_0 + N_i)$ of O and O^+ , 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 53.2 kPa. The graph shows that oxygen is already fully ionized at thermal energies well below the first ionization energy of 13.618 eV (equivalent to 158 000 K). If we consider a temperature of 23 000 K, the ionization degrees of O

and O^+ obtained by means of the Saha equation (8) are 0.994 and 0.022, respectively. For $T = 31\,500$ K, the ionization degrees of O and O^+ obtained by means of the Saha equation (8) are 0.999 and 0.34, respectively. These so high values of the ionization degrees justify the observed emission spectra.

3.5. Electron number density

The evolution of the laser plasma can be divided into several transient phases. The initial plasma (~ 0 –100 ns) is characterized by high electron and ion densities (10^{17} – 10^{20} cm^{-3}) and temperatures around 40 000 K. Of course, the density gradient of the plasma is the 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 ion in the plasma. Structured emission spectra from atomic and ionized species can be found after ~ 300 ns delay. The observed spectral lines are always broadened, partly due to the finite resolution of the spectrometer and partly due 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 (in Å) $\Delta\lambda_{FWHM}^D = 7.16 \times 10^{-7} \cdot \lambda \cdot \sqrt{T/M}$, with λ the wavelength in Å, T the temperature of the emitters in K and M the atomic mass in amu. The Doppler line widths for some lines of O^+ for different temperatures are shown in figure 6. In our experiments, for O^+ lines, the Doppler line widths are 0.07–0.12 Å at 23 000 K.

Owing to the high electron densities in LIBS experiments, the emission lines are mainly broadened by the Stark effect. Both ions and electrons produce Stark broadening, but electrons are responsible for the major part because of their higher relative velocities. Stark broadening produces Lorentzian line shapes, except at the line centre, where electrostatic interactions with ions cause a dip. The FWHM

Figure 6. Doppler line widths for some lines of O^+ .

of the Stark broadened lines is related to the electron number density n_e (cm^{-3}) by [31]

$$\Delta\lambda_{\text{FWHM}}^S = 2W \left(\frac{n_e}{10^{16}} \right) + 3.5A \left(\frac{n_e}{10^{16}} \right)^{1/4} \times (1 - BN_D^{-1/3})W \left(\frac{n_e}{10^{16}} \right), \quad (9)$$

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:

$$N_D = 1.72 \times 10^9 \frac{T^{3/2}}{n_e^{1/2}}. \quad (10)$$

The electron and 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 LIB conditions Stark broadening is predominantly by electron impact, the ion correction factor can safely be neglected, and equation (9) becomes

$$\Delta\lambda_{\text{FWHM}}^S = 2W \left(\frac{n_e}{10^{16}} \right). \quad (11)$$

The choice of plasma emission for n_e measurements is made to ensure that the O^+ spectral lines are sensitive enough to 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 O^+ (2738, 3386, 3809, 4075 and 4418 Å) from the high-resolution spectra. The electron impact parameters for the different O^+ lines were approximated to a first-order exponential decay. The electron number densities of the laser-induced plasma were determined from the high-resolution emission spectra in oxygen at a pressure of 48.8 kPa, excited by the CO_2 laser at 10.591 μm with a power density of 4.28 GW cm^{-2} . 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 [32]. Electron densities in the range $(3.5\text{--}16.5) \times 10^{16} \text{ cm}^{-3}$, with an estimated uncertainty of 10%, were determined from the Stark broadening data of several singly ionized oxygen lines. The validity criteria for LTE and, consequently, criteria for the application of the different spectroscopic methods are extensively discussed in the literature [33, 34]. For the LTE, the excited states have to be populated through collisions. Using McWhirter's criterion [34] to check the condition for the validity of the LTE, we find that the electron number density satisfies

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

Here, n_e (cm^{-3}) is the electron density, T (K) is the plasma temperature and ΔE (eV) is the difference in the energies between the upper and lower states of all the O^+ investigated transitions. At the evaluated temperature of $23\,000 \pm 3000$ K, equation (12) yields $n_e \approx (0.54\text{--}2.3) \times 10^{16} \text{ cm}^{-3}$. These electron densities are lower than the deduced values from the Stark broadening $(3.5\text{--}16.5) \times 10^{16} \text{ cm}^{-3}$, approximately one order of magnitude. Based on these calculations, the validity of the LTE assumption is supported.

3.6. Effect of laser wavelength and irradiance

The interactions between the incoming laser radiation and the gas sample depend upon numerous variables related to the laser and the gas. These variables include laser wavelength, energy, spatial and temporal profile of the laser beam and the thermal properties of the sample. The incident beam is partially reflected and partially absorbed by the bulk to a degree that depends on the nature of the gas and the temperature it reaches under laser irradiation.

LIBS spectra obtained by laser irradiation at different wavelengths are compared in figure 7. These high-resolution LIB emission spectra in oxygen were obtained to a pressure of 48.8 kPa, excited by two TEA- CO_2 laser wavelengths at 10.591 μm ($I_W = 6.31 \text{ GW cm}^{-2}$) and 9.621 μm ($I_W = 5.36 \text{ GW cm}^{-2}$). The spectral range was chosen in order to detect both single and double ionized oxygen species. Also this spectral region has been selected to show differences in signal intensity and background emission in detail. The first remark that we should make is that the background continuum emission after the same optimization performed on the data acquisition window is much stronger for the spectrum produced by the 10.591 μm laser line. This is due to the higher laser power density ($I_W = 6.31 \text{ GW cm}^{-2}$) and the higher absorption in the plasma caused by the inverse bremsstrahlung, whose cross-section is proportional to $\lambda^3 [1 - \exp(-hc/\lambda k_B T)]^{-1}$ or approximately λ^2 (T is the electron temperature during the electron avalanche or cascade growth of ionization and λ is the laser excitation wavelength). The spectral lines of O^+ and O^{2+} (2983.78, 3017.63, 3023.45, 3043.02, 3047.13, 3059.30 Å) were clearly observed. It is clear that the ionic spectral lines for both O^+ and O^{2+} were

Figure 7. High-resolution LIB emission spectra in oxygen at a pressure of 48.8 kPa, excited by two TEA-CO₂ laser wavelengths at 10.591 μm ($E_W = 3161$ mJ) and 9.621 μm ($E_W = 2685$ mJ).

enhanced by a factor of 4 when the LIBS is induced by the TEA-CO₂ laser at 10.591 μm . Besides, the irradiation at this wavelength favours the formation of doubly ionized species ($\sim 30\%$), as it is obtained from the ratio of the intensities of the O²⁺ and O⁺ lines. Moreover, plasma electron densities were determined from Stark broadening of the O²⁺ double ionized line at 2983.78 Å. The measured electron densities for the LIB emission spectra in oxygen were $(3.5 \pm 0.2) \times 10^{16} \text{ cm}^{-3}$ and $(3.2 \pm 0.2) \times 10^{16} \text{ cm}^{-3}$ for excitation at 10.591 μm and 9.621 μm , respectively. Values of the electron impact half-width W for O²⁺ were taken from the reported values given by Sreckovic *et al* [35]. It is noted that the emission intensity for O⁺ and O²⁺ shows a different picture from the electron density possibly due to the effect of the laser wavelength. To see the effect of laser irradiance the measurements were also carried out at different laser fluences. Optical emission spectra of the oxygen plasma plume at a pressure of 48.8 kPa as a function of the laser intensity are shown in figures 8(a) and (b). These spectra were recorded after the incidence of only one pulse of the TEA-CO₂ laser. The data were measured at a delay of 20 ms. An increase in atomic/ionic emission intensity and in the doubly ionized O²⁺ formation with respect to O⁺ with increasing laser irradiance was observed. Also the background increases with the laser power. At higher laser power densities ($6.31\text{--}4.28 \text{ GW cm}^{-2}$), the spectral lines are more broadened than at lower power densities as a result of the high pressure associated with the plasma. It is assumed that at a higher laser fluence the LIB plasma is more energetic and more ionized.

3.7. Effect of oxygen pressure on the plasma

The emission characteristics of the laser-induced plasma are influenced by the composition of the gas atmosphere. The pressure of the gas is one of the controlling parameters of the plasma characteristics, as well as the factors related to the laser energy absorption. Also the presence of air gas (vacuum

conditions) during the LIB process has consequences on the expansion dynamics. An interesting observation was the effect of the oxygen pressure. Nanosecond TEA CO₂ laser produced plasma emission has been characterized as a function of oxygen pressure. Experiments were performed in the pressure interval from 8 to 50 kPa and at a pulse energy of 3161 mJ. Figure 9 shows LIB emission spectra at various oxygen pressures, excited by the 10.591 μm line at a power density of 6.31 GW cm^{-2} . As can be seen in figure 9, the intensities of different spectral lines of O⁺ and O²⁺ increase with decreasing pressure, reach a maximum at about 12.5 kPa and then decrease for lower pressures. Characteristic emission lines from O⁺ and O²⁺ elements exhibited significant enhancement in the signal intensity at a few kPa oxygen pressure as compared with high pressures below atmospheric pressure. However, the ratio of the intensities among the O²⁺ and O⁺ lines remains the same at all pressures. The measurements indicate enhancement due to a longer lifetime of the plasma expanding to a larger size at lower oxygen pressures. Further reduction in oxygen pressure down to ~ 12.5 kPa resulted in a decrease in signal intensity, as a result of a reduction in collisional excitation of the emission lines which occurs when the plasma plume expands into the oxygen atmosphere.

3.8. Optical breakdown threshold intensities for O₂

The strong atomic and ionic lines observed in LIBS spectra of oxygen indicate the high degree of excitation/ionization and the high rate of the O₂ dissociation process achieved in the plasma. When a high-power laser beam of intensity I_W interacts with a gas, electrons involving the formation of laser-induced plasma can be generated through two main processes: multiphoton ionization (MPI) and electron impact ionization both followed by electron cascade. While the MPI process is self-sufficient, the electron impact ionization requires the presence of seed electrons in the laser focal region. The MPI process [$n\hbar\nu + A \rightarrow A^+ + e + I_P(A)$; $n\hbar\nu \geq I_P(A)$] involves the simultaneous absorption of a number of photons required to equal the IP of a gas. The ionization rate in MPI varies as I_W^n where n is the number of photons needed to strip off an electron, which corresponds to the integer part of the quantity:

$$n = \frac{I_P + \varepsilon_{\text{osc}}}{h\nu} + 1, \quad (13)$$

with ε_{osc} the oscillation energy of a free electron in the alternating electric field. Within the classical microwave breakdown theory [36], a free electron oscillates in the alternating electric field E of the laser electromagnetic wave (with frequency ω and wavelength λ), and its oscillation energy,

$$\begin{aligned} \varepsilon_{\text{osc}}[\text{eV}] &= \frac{e^2 E^2}{4m\omega^2} = \frac{e^2}{4m\pi c^3} I_W \lambda^2 \\ &= 4.67 \times 10^{-14} I_W [\text{W cm}^{-2}] \lambda^2 [\mu\text{m}], \end{aligned} \quad (14)$$

remains constant. On the other hand, MPI is relatively improbable for oxygen atoms or molecules in the ground state [O($2s^2 2p^4 \ ^3P_2$) and O₂($X \ ^3\Sigma_g^-$)], since their high IPs (13.618 eV and 12.070 eV, respectively) mean that 117 photons

Figure 8. (a)–(b) High-resolution LIB in oxygen (at a pressure of 48.8 kPa) emission spectra observed in the (a) 3957–4085 Å and (b) 4195–4310 Å regions, excited by two TEA-CO₂ laser wavelengths at 10.591 μm as a function of the laser power density.

and 104 photons ($\lambda = 10.591 \mu\text{m}$), respectively, are required for these processes. The probability of MPI W_{MPI} , by absorbing simultaneously n laser photons to strip off an electron, is expressed by the classical formula [37, 38]

$$W_{\text{MPI}}[\text{s}^{-1}] \cong \omega n^{3/2} \left(1.36 \frac{\varepsilon_{\text{osc}}}{I_P} \right)^n$$

$$= 1.88 \times 10^{15} \lambda^{2n-1} [\mu\text{m}] n^{3/2}$$

$$\times \left\{ \frac{6.35 \times 10^{-14} I_W [\text{W cm}^{-2}]}{I_P [\text{eV}]} \right\}^n. \quad (15)$$

Besides, the probability of simultaneous absorption of photons decreases with the number of photons n necessary to cause ionization. In general, this probability is $W_{\text{MPI}} \propto \Phi_W^n \propto F_E^{2n}$. Calculations of MPI probability for O₂ give $W_{\text{MPI}} = 4.6 \times 10^{-236} \text{ s}^{-1}$ for the CO₂ laser at $\lambda = 10.591 \mu\text{m}$ and $I_W = 6.31 \text{ GW cm}^{-2}$ ($n = 104$). For example, for a 193 nm (ArF) at the laser intensity $I_W = 1 \text{ GW cm}^{-2}$ ($n = 2$), the probability of MPI for O₂ gives $W_{\text{MPI}} = 1058 \text{ s}^{-1}$. Electron impact ionization process consists of the absorption of light photon by free or quasifree electrons ($e + n h \nu + A \rightarrow e^* + A$). These free or quasifree electrons can be produced by the effect of cosmic ray ionization (natural ionization), by means of MPI or by a breakdown induced in some gas impurity. In air at atmospheric pressure, the natural electron density is $\sim 10^3 \text{ cm}^{-3}$. These electrons in the focal volume gain sufficient energy, from the laser field through inverse bremsstrahlung collision with neutrals, to ionize oxygen atoms, molecules or ions by inelastic electron–particle collision resulting in two electrons of lower energy being available for starting the process again $\{e^*[\varepsilon^3 I_P(A)] + A \rightarrow A^+ + 2e; e^*[\varepsilon^3 I_P(A^+)] + A^+ \rightarrow A^{2+} + 2e, \text{ etc}\}$. Electron impact ionization is most important for the longer wavelengths used in this work ($\lambda = 9.621$ and $10.591 \mu\text{m}$). The observed ionic emissions are best explained by an electron impact ionization mechanism. The

Figure 9. High-resolution LIB emission spectra at various oxygen pressures, excited by the TEA-CO₂ laser (10.591 μm) at a power density of 6.31 GW cm⁻².

main role for MPI in our experimental conditions is to create seed electrons in the plasma plume.

On the other hand, we have made experimental measurements of breakdown threshold laser intensities of oxygen. The minimum optical laser power density required to form a plasma is called the breakdown threshold. The threshold power density is dependent on the kind of laser, laser wavelength, pulse length, beam size of the focal volume and gas pressure. Breakdown thresholds of solids and liquids are usually lower than for gases. Several LIB threshold measurements have been reported for oxygen [22–27] using CO₂ [22] and Nd:YAG [23–27] lasers. The breakdown threshold was defined as the laser energy at which the gas would break down on more than 50% of the laser shots.

Figure 10. Experimental laser-induced breakdown thresholds in oxygen for different pressures. Solid circle: without previous breakdown; open triangle: after previous breakdown.

In the experimental section we explain the two methods that have been used to measure the breakdown threshold of oxygen. Some authors induce the breakdown at a pressure over the desired value, later the pressure is lowered and the energy adjusted until the breakdown begins with some probability, usually around 50% [26, 27]. This method is similar to inducing the breakdown with energy in excess and to attenuating the laser until the spark disappears. In these cases it could be that initial free electrons have been produced by previous breakdowns and they are the seeds of the avalanche process. Another way to induce the breakdown is to fix the pressure and to gradually increase the energy until a visible spark is observed around the focal region at the determined number of laser pulses [22]. In this last method the obtained threshold value is normally higher. We have used both methods to measure the oxygen breakdown at several pressures ($\lambda = 10.591 \mu\text{m}$) and the results are shown in figure 10. As can be seen from figure 10, if a breakdown has been previously induced in the gas (open triangles), the pressure range to induce the breakdown is bigger and the power density is approximately half than when no previous breakdown is induced (solid circles). The number of free electrons is higher in conditions of previous breakdown than in the case of no previous breakdown, lowering the threshold for the plasma initiation. This behaviour has been observed by different authors. Dewhurst [23] reported a decrease in the breakdown threshold intensity from $\sim 1.8 \times 10^{14}$ to $\sim 1.2 \times 10^{14} \text{ W cm}^{-2}$ at $0.69 \mu\text{m}$ and $\sim 5.5 \times 10^{13}$ to $\sim 1 \times 10^{13} \text{ W cm}^{-2}$ at $0.53 \mu\text{m}$ for oxygen pressures between ~ 200 and ~ 8000 Torr. Chang *et al* [22] reported for several gases (O_2 , N_2 , air, He and Ne) that the threshold power density decreases as the pressure increases and that it decreases as the focal volume increases. They reported a slow decrease with a little minimum of the breakdown threshold intensity from $\sim 15 \times 10^9$ to $\sim 5 \times 10^9 \text{ W cm}^{-2}$ at a diffusion length of $\Lambda = 1.6 \times 10^{-3} \text{ cm}$ and from $\sim 3 \times 10^9$ to $\sim 2 \times 10^9 \text{ W cm}^{-2}$ at a diffusion length of $\Lambda = 3.2 \times 10^{-3} \text{ cm}$ for oxygen pressures between ~ 200 and ~ 10000 Torr. In this work, they used a

CO_2 laser and the focal diameter range from 0.75×10^{-2} to $3 \times 10^{-2} \text{ cm}$. Phuoc [27] reported a decrease in the breakdown threshold intensity from $\sim 1 \times 10^{13}$ to $\sim 2 \times 10^{12} \text{ W cm}^{-2}$ at $0.532 \mu\text{m}$ and from $\sim 8 \times 10^{12}$ to $\sim 1 \times 10^{12} \text{ W cm}^{-2}$ at $1.064 \mu\text{m}$ for oxygen pressures between 150 and 3040 Torr. It is to be noted that we have obtained similar threshold power densities for O_2 to those given by Chang [22], but lower values than those reported in [23–27]. This fact can be related in part to the used focal length (24 cm) and beam size in the focal region ($7.85 \times 10^{-3} \text{ cm}^2$) that is one order of magnitude, at least, higher than the values commonly used in the literature, favouring the probability of the existence of free electrons to seed the process and decreasing the threshold laser intensity due to the lack of diffusion losses.

It has been established [3–11] that the threshold photon flux density or equivalently the threshold power density for MPI varies with $P^{-1/n}$, where P is the gas pressure and n is the number of simultaneously absorbed photons. Therefore, MPI predicts a very weak dependence of the threshold power density on pressure. The measurements of the breakdown threshold intensity variation with the oxygen pressure (figure 10) reveal the weak pressure dependence, a characteristic of MPI. Our investigations of the threshold power densities covered the pressure range $P < 65 \text{ kPa}$ without previous breakdown and $P < 75 \text{ kPa}$ after previous breakdown. This pressure range is relatively limited due to the characteristics of the employed pyrex gas cell. Presumably, we suppose that the oxygen breakdown occurs in the high pressure range taking into account the experimental observations reported by Chan *et al* [22], Dewhurst [23], Stricker and Parker [24], Gamal [25] and Phuoc [26, 27]. Therefore, starting from our experimental observations and calculations, we can conclude that although the measurements of the breakdown threshold intensity variation with the oxygen pressure (figure 10) reveal the weak pressure dependence, a characteristic of MPI, our calculations of MPI probability for O_2 give $W_{\text{MPI}} \cong 0$ for the CO_2 laser at $\lambda \cong 10 \mu\text{m}$ and $I_w \cong 6 \text{ GW cm}^{-2}$. So we think that although the first electrons must appear via MPI or natural ionization, ionization by electron impact is the main mechanism responsible for the breakdown in molecular oxygen.

The condition for optical breakdown is taken to occur when the number density of the induced electrons equals the critical density for the laser wavelength. The critical plasma density $n_e^{\text{crit}} [\text{cm}^{-3}] = m_e \omega^2 / 4\pi e^2 \cong 1.1 \times 10^{21} / \lambda^2 [\mu\text{m}]$ ($n_e^{\text{crit}} \cong 10^{19} \text{ cm}^{-3}$ for CO_2 laser) is the density where the electron plasma frequency equals the laser frequency. When the electron density exceeds the critical density the sample is not transparent any more. Energetic electrons produce excited species through impact excitation, dissociation and ionization of O_2 molecules. The initial formed plasma expands within the space and supplies the spark gap with sufficient electrons, ionizing the gas and drastically reducing its electrical resistance; therefore, the breakdown occurs at electric fields less than the self-breakdown electric field of the threshold. The plasma is confined within a high-density shell of neutral oxygen gas that traps ionizing radiation in a region of low E/N (where E is the applied electric field divided by the total gas

mixture density N); therefore inhibiting further expansion by non-hydrodynamic means electron avalanche. The reduced electric field E/N (or equivalently E/P where P is the pressure; $P = Nk_B T$) gives an idea about the average energy that an electron possesses in plasma. The greater the value of E/N (higher E and/or lower N) the further apart is the average energy of the electrons from oxygen molecules. The non-equilibrium highly transient plasma (or plasma during its formative non-equilibrium phase), which is generated in E/N conditions and applied during its formative phase, allows radicals (O , O^+ and O^{2+}) and other electronically excited species (N , N^+ and N_2^+) to be generated over a relatively large volume. Active radical generation is due to molecule dissociation and excitation by electrons in the laser electric field, radiation and more complex processes. The presence of radicals or excited molecules can effectively improve ignition conditions but the problem is at the level of the required laser power density. If the electron cascade processes and chain chemical reactions are realized, the production of even a small number of free electrons and radicals can lead to a large benefit in total reaction rates, as well as diminishing of the required laser power density input. The key for transient plasma is the high magnitude of the local reduced electric field E/N that is associated at the laser focal volume which may produce electrons in energies of about 10–15 eV or more and which increases the probability of molecular oxygen dissociation significantly. Energetic electrons with high kinetic energies can effectively generate reactive species, which can then rapidly initiate or accelerate chain reactions. Generally speaking, any type of excitation (dissociation, ionization, electron excitation or vibrational excitation) affects the reaction rates positively, improving ignition conditions. The electron impact process is effective for a high magnitude of the reduced electric field E/N .

4. Conclusions

Laser-induced breakdown generated by CO₂ laser pulses ($\lambda = 9.621$ and $10.591 \mu\text{m}$; $\tau_{\text{FWHM}} = 64$ ns; power densities ranging from 0.87 to 6.31 GW cm^{-2}) in oxygen has been investigated by means of OES. The plasma produced in oxygen gas and pressures ranging from 4.6 to 75 kPa has been measured and analysed. The strong emission observed in the plasma region is mainly due to the relaxation of excited atomic O and ionic fragments O^+ and O^{2+} . Excitation temperatures of $31\,500 \pm 1600$ K and $23\,000 \pm 3000$ K were estimated by means of O^{2+} and O^+ ionic lines, respectively. Electron number densities of the order of $(3.5\text{--}16.5) \times 10^{16} \text{ cm}^{-3}$ were deduced from the Stark broadening of several ionic O^+ lines. The characteristics of the spectral emission intensities from different species have been investigated as functions of the oxygen pressure and laser irradiance. Optical breakdown threshold intensities in O₂ at $10.591 \mu\text{m}$ have been determined. On the basis of our observations and calculations we propose that although the first electrons must appear via MPI of any molecular species present in the focal volume, or by natural ionization, electron impact is the main mechanism responsible for the breakdown in molecular oxygen.

Acknowledgments

The authors acknowledge the support received in part by the DGICYT (Spain) Projects: MEC: CTQ2007-60177/BQU and MEC: CTQ2008-05393/BQU for this research.

References

- [1] Emsley J 2001 'Oxygen', *Nature's Building Blocks: An A–Z Guide to the Elements* (Oxford, UK: Oxford University Press) pp 297–304
- [2] Maker P D, Terhune R W and Savage C M 1963 *Proc. 3rd Int. Conf. Quantum Electronics* (Paris: Dunod) vol 2 p 1559
- [3] Zeldovich Y B and Raiser Y P 1965 *Sov. Phys.—JETP* **21** 190
- [4] Bebb H B and Gold A 1966 *Multiphoton Ionization of Hydrogen and Rare Gas Atoms, Physics of Quantum Electronics* ed P L Kelly *et al* (New York: McGraw-Hill)
- [5] Demichelis C 1969 *IEEE J. Quantum Electron.* **5** 188
- [6] Isenor N R and Richardson M C 1971 *Appl. Phys. Lett.* **18** 224
- [7] Lyman J L and Jensen R J 1972 *Chem. Phys. Lett.* **13** 421
- [8] Morgan C G 1975 *Rep. Prog. Phys.* **38** 621
- [9] Cantrell C D, Freund S M and Lyman J L 1979 *Laser Induced Chemical Reactions and Isotope Separation in Laser Handbook* vol 3b ed M L Stich (Amsterdam: North-Holland)
- [10] Lyman J L, Quigley G P and Judd O P 1980 *Multiple-Photon Excitation and Dissociation of Polyatomic Molecules* ed C D Cantrell (Berlin: Springer)
- [11] Hermann J and Floch T L 2004 *J. Appl. Phys.* **96** 3084
- [12] Bekefi G 1976 *Principles of Laser Plasma* (New York: Wiley)
- [13] Radziemski L J and Cremers D A 1989 *Laser Induced Plasma and Applications* (New York: Dekker)
- [14] Majidi V and Joseph M R 1992 *Crit. Rev. Anal. Chem.* **23** 143
- [15] Yueh F-Y, Singh J P and Zhang H 2000 *Encyclopedia of Analytical Chemistry (Laser-Induced Breakdown Spectroscopy, Elemental Analysis)* ed R A Meyers (Chichester: Wiley)
- [16] Cremers D A and Radziemski L J 2006 *Handbook of Laser-Induced Breakdown Spectroscopy* (Chichester: Wiley)
- [17] Miziolek A W, Palleschi V and Schechter I 2006 *Laser-Induced Breakdown Spectroscopy* (Cambridge: Cambridge University Press)
- [18] Pasquini C, Cortez J, Silva L M C and Gonzaga F B 2007 *J. Braz. Chem. Soc.* **18** 463
- [19] Camacho J J, Poyato J M L, Díaz L and Santos M 2007 *J. Phys. B: At. Mol. Opt. Phys.* **40** 4573
- [20] Camacho J J, Poyato J M L, Díaz L and Santos M 2007 *J. Appl. Phys.* **102** 103302
- [21] Camacho J J, Díaz L, Santos M, Reyman D and Poyato J M L 2008 *J. Phys. D: Appl. Phys.* **41** 105201
- [22] Chan C H, Moody C D and McKnight W K 1973 *J. Appl. Phys.* **44** 1179
- [23] Dewhurst R J 1978 *J. Phys. D: Appl. Phys.* **11** L191
- [24] Stricker J and Parker J G 1982 *J. Appl. Phys.* **53** 851
- [25] Gamal Y E E-D 1988 *J. Phys. D: Appl. Phys.* **21** 1117
- [26] Phuoc T X 2000 *Opt. Commun.* **175** 419
- [27] Phuoc T X and White C M 2000 *Opt. Commun.* **181** 353
- [28] Nordstrom R J 1995 *Appl. Spectrosc.* **49** 1490
- [29] NIST Atomic Spectra Database online at <http://physics.nist.gov/PhysRefData/ASD/index.html>
- [30] Martin W C and Zalubas R 1983 *J. Phys. Chem. Ref. Data* **12** 323
- [31] Griem H R 1974 *Spectral Line Broadening by Plasmas* (New York: Academic)

- [32] Griem H R 1964 *Plasma Spectroscopy* (New York: McGraw-Hill)
- [33] Griem H R 1997 *Principles of Plasma Spectroscopy* (Cambridge: Cambridge University Press)
- [34] McWhirter R W P 1965 *Plasma Diagnostic Techniques* ed R H Huddleston and S L Leonard (New York: Academic) chapter 5
- [35] Sreckovic A, Dimitrijevic M S and Djenize S 2001 *Astron. Astrophys.* **371** 354
- [36] MacDonald A D 1966 *Microwave Breakdown in Gases* (New York: Wiley)
- [37] Raizer Y P 1991 *Gas Discharge Physics* (Berlin: Springer)
- [38] Luther-Davies B, Gamaly E G, Wang Y, Rode A and Tikhonchuk V T 1992 *Sov. J. Quant. Electron.* **22** 289