Abstract The effect of introducing molecular compounds into argon plasmas has been studied using an expanding microwave induced plasma at atmospheric pressure. Besides the use of optical emission spectroscopy (OES), also the time dependent behavior of line intensities during power interruptions has been studied. From the measurements it is found that even an injection of small amounts of molecular compounds (> 0.5%) leads to important changes in excitation mechanisms in the plasma. It is also found that in the recombination zone downstream in the plasma an excitation mechanism which is independent of the electron density, e.g. excitation transfer from metastables or Penning ionization, must be responsible for the excitation of analytes.

1 Introduction

The injection of aerosols or molecular gases into argon discharges has a strong impact on excitation mechanisms in these plasmas and can both effect the electron density and electron temperature. When using a plasma as radiation source in spectrochemical analysis, usually easy ionizable elements (EIEs) are introduced as well. One should be aware that this might lead to non-linearities or matrix effects. Therefore, it is important to study changes in the Atomic State Distribution Function (ASDF) due to the introduction of such EIEs or molecular species.

Studies have been performed on atmospheric argon plasmas produced by the “TIA” (“Torche à Injection Axiale”) [1, 2], an atmospheric microwave induced plasma torch. Due to different design features, the much higher operational frequency (2.45 GHz) and the much smaller plasma dimensions, plasmas produced by the TIA have different characteristics than Inductively Coupled Plasmas (ICPs) and reasearch is necessary in order to obtain more knowledge about the involved plasma processes. Several experimental results have been compared with results obtained from an ICP.

Two different techniques have been used to obtain more insight in molecular processes and changes in excitation mechanisms due to introduction of analytes or molecular gases (air or carbon dioxide):

- optical emission spectroscopy (OES),
- power interruption experiments.

The first technique provides information about the dissociation and association processes inside the plasma, especially after introducing molecular species. The latter technique, in which the time dependent behavior of emission lines during a temporarily removal of the power input to the plasma is studied, provides information about dominant population mechanisms of radiative levels. Both techniques and their results will be presented separately.

2 Optical emission spectroscopy

2.1 Instrumental

The plasmas are produced by the TIA (from “Torche à Injection Axiale”), a high power microwave induced plasma torch, developed by Moisan et al. in 1993 [1]. The plasma carrier gas and aerosols are introduced through the gas channel in the nozzle. Using an argon gas flow [Ar] = 3 L · min⁻¹, no analyte introduction and a power input P = 1 kW, plasmas are typically 5 cm high and have a diameter of 2–3 mm. Compared to the ICP the diameter of the plasma is very small. This is not only due to the small diameter of the nozzle (= 1.8 mm) and flow aspects, but also due to the small skin depth of microwave radiation (approximately 0.1 mm at 2.45 GHz in argon plasmas). It should be noted that the plasma is freely expanding and has direct contact with the ambient air under normal operational conditions.
The setup is presented in Fig. 1. Microwave energy is generated by a magnetron and is transported towards the plasma torch through a WR-340 waveguide. Impedance matching and tuning can be achieved by a triple stub tuner, a movable plunger and several tuning elements inside the TIA. Basically, inside the TIA the propagation mode of the microwave radiation is converted from the TE\textsubscript{01} mode inside the rectangular waveguide into the coaxial TEM mode. Energy is dissipated on top of the nozzle where the plasma is created. The emission of the plasma is recorded with the aid of a 1 m monochromator (1200 gr/mm grating) with a UV-enhanced CCD camera in the exit plane. Measurements have been performed using the so-called spectroscopic mode, in which the 2D camera is used as a 1D array of 750 pixels, each 11.5 \textmu m \times 6.53 mm. With the optics a spectral wavelength interval of typically 5-8 nm can be recorded simultaneously within the range of 200 to 1000 nm.

In Table 1 the major components used for the experiments (including the power interruption experiments, cf. §3) are given.

### 2.2 Experimental results

To study molecular processes in an argon discharge, experiments with the molecular gases CO\textsubscript{2} and air and aqueous aerosols have been performed. It is found that if CO\textsubscript{2} is introduced into an argon plasma, the spectrum is dominated by molecular bands generated by diatomic association products. Emission from CN is by far dominant and can readily be observed directly above the nozzle, indicating that the dissociation of CO\textsubscript{2} and the creation of new species are almost instantaneous processes, cf. Fig. 2. It should be noted that the height dependence of the normalized intensities of dissociation and association products are similar to the height dependence of the normalized intensity of a low lying argon line (763.51 nm, 4p-4s).

In Table 2 the molecular bands are listed, which are present between 200 and 1000 nm. Even if there is no deliberate introduction of carbon dioxide most of these bands are still weakly present. The reason can be found in the entrainment of ambient air and impurities in the argon gas. It should be noted that emission of CO\textsubscript{2} or CO is not present. The observed molecular bands are well-known from ICP-AES [3, 4] although their intensities are usually lower due to the relatively small amounts of air entrainment into the ICP. In order to reduce interference of analyte lines with molecular bands many efforts have been

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**Table 1** Instrumental components used for the spectroscopic measurements and the power interruption experiments

<table>
<thead>
<tr>
<th>Components</th>
<th>Model and Details</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetron + power supply</td>
<td>MW-GIR2M130-2K (( P_{\text{max}} = 2 \text{ kW} ))</td>
<td>Muegge (Germany)</td>
</tr>
<tr>
<td>Plasma source</td>
<td>TIA (Torche à Injection Axiale)</td>
<td>Laboratory built</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Monospek 1000, 1200 gr/mm, 420 nm blaze-angle</td>
<td>Jobin Yvon</td>
</tr>
<tr>
<td>CCD camera(^{a})</td>
<td>ST6-UV</td>
<td>Santa Barbara Instrument Group</td>
</tr>
<tr>
<td>Photo multiplier tube</td>
<td>R376, Head-on</td>
<td>Hamamatsu</td>
</tr>
<tr>
<td>Amplifier(^{b})</td>
<td>R376, Head-on</td>
<td>Phillips</td>
</tr>
<tr>
<td>Discriminator(^{b})</td>
<td>R376, Head-on</td>
<td>Phillips</td>
</tr>
<tr>
<td>Multi-channel scaler(^{b})</td>
<td>Ortec ACE-MCS, 24 bits, 4096 counters, 2 \mu s resolution</td>
<td>EG &amp; G</td>
</tr>
<tr>
<td>Mass flow controllers</td>
<td>FC-260 series</td>
<td>Tylan General</td>
</tr>
</tbody>
</table>

\(^{a}\) Used for OES measurements only

\(^{b}\) Used for power interruption experiments only
made to reduce molecular emission, e.g. by using gas mix-
tures instead of argon only [5].

The very intense radiation of CN when CO₂ and of NH
when water is introduced (c.f. Table 2) indicate a strong
interaction of the plasma with the ambient air. The pene-
tration of nitrogen provides an extra destruction channel
for charged particles due to its quasi-resonant charge trans-
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and nitrogen are 15.76 and 15.68 eV, respectively):
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\text{Ar}^+ + \text{N}_2 \rightarrow \text{Ar} + \text{N}_2^+ . \tag{1a}
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This CT is easily followed by dissociative recombina-
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Fig. 2 Normalized intensities of several dissociation and associa-
tion products after introduction of CO₂ into an argon discharge as
a function of the height above the nozzle (AN). As a reference an
argon line is given. Measurements are “side-on” measurements and
integrated over the total plasma diameter

Table 2 Observed molecular spectra from discharges in ar-
gon or mixtures of argon and carbon dioxide and/or H₂O

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Emission bands</th>
<th>Transition</th>
<th>Energy (eV)</th>
<th>Relative intensity</th>
</tr>
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<tbody>
<tr>
<td>CN</td>
<td>Violet system</td>
<td>B₂Σ→A²Πi</td>
<td>3.20→1.15</td>
<td>very intense+a</td>
</tr>
<tr>
<td>C₂</td>
<td>Swan system</td>
<td>A³Π→X²Σ⁺</td>
<td>2.40→0</td>
<td>weakb</td>
</tr>
<tr>
<td>NH</td>
<td>First positive system</td>
<td>B²Π→A²Σ</td>
<td>7.42→6.24</td>
<td>very weak</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>Second positive system</td>
<td>C³Π→B²Πı</td>
<td>11.08→7.42</td>
<td>weak</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>First negative system</td>
<td>B₂Σ⁺→X²Σ⁺</td>
<td>3.17→0</td>
<td>intense</td>
</tr>
<tr>
<td>NO</td>
<td>First positive system</td>
<td>B₂Σ→X²Πi</td>
<td>5.47→0</td>
<td>weak</td>
</tr>
<tr>
<td>OH</td>
<td>3064 Ångström system</td>
<td>A²Σ→X²Πi</td>
<td>4.46→0</td>
<td>weakc</td>
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+a Rather weak in pure argon discharge
+b Absent in pure argon discharges
+c Very intense after aqueous analyte introduction

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tron density, they may have a significantly higher proba-
0.2 L·min⁻¹ and 30% versus 0.7%, respectively). This difference is partly determined by the capability of the plasma source to adjust automatically for impedance changes. For the ICP this capability is limited whereas for the TIA changes in the plasma impedance have less influence on the energy transfer from the generator towards the plasma region. Also the electron temperature is much higher in an argon plasma produced by the TIA. Therefore the introduction of a small amount of molecules has less impact on the electron density. This makes the TIA favorable in case molecular gases with a strongly varying composition, such as flue gases, have to be analyzed [9].

### 3 Power interruption experiments

#### 3.1 Theory and instrumental

By studying the time dependent behavior of atomic line or molecular band intensities during power interruptions of the plasma power supply, information can be obtained about the excitation mechanisms governing the atomic state distribution function (ASDF).

Microwave energy will mainly be absorbed by electrons which on their turn will heat the heavy particles. Since this is a relatively inefficient process due to the large difference in mass, the heavy particle temperature $T_h$ will remain lower than the electron temperature $T_e$ (for argon plasmas produced by the TIA 0.4 and 1.7 eV, respectively [10]). The heavy particles are finally cooled by the surroundings. This can be presented by the energy flow diagram.

μwave energy → electrons → heavy particles → surroundings

If the microwave energy is suddenly removed, this will first affect the electrons. Within a very short time (< 1 μs) they will largely thermalize with heavy particles and will therefore be cooled down towards a temperature close to $T_h$ [11, 12].

This instantaneous decrease in $T_e$ will affect the densities of excited states. In case a level $p$ is mainly populated by electron impact from the atom ground state, its behavior is dominated by the Boltzmann balance

\[
A_1 + e_{\text{fast}} \xrightleftharpoons{\text{Boltzmann}} \rightarrow A_p + e_{\text{slow}}
\]

of excitation (to the right) and deexcitation (to the left). Due to the decreased number of fast electrons, the Boltzmann balance will shift to the left and the density of excited state $p$ decreases. As a result emission from level $p$ will decrease as well.

Highly excited argon states which are close to the ion ground state are often dominated by the Saha balance of ionization and (three particle) recombination:

\[
A_p + e_{\text{fast}} \xrightleftharpoons{\text{Saha}} \rightarrow A^+ + e_{\text{slow}} + e_{\text{slow}}
\]

For these states the reduction of fast electrons leads to a temporarily increase of their population because the balance shifts to the left. Since the population increases, emission from the concerned levels will increase as well.

After a few μs the losses of electrons and ions due to recombination and diffusion processes will become dominant and line intensities will drop.

Other excitation balances which can be distinguished are excitation transfer (ET)

\[
A_p + X_r \xrightleftharpoons{\text{ET}} \rightarrow A_q + X_s
\]

or charge transfer (CT)

\[
A^+ + X \xrightleftharpoons{\text{CT}} \rightarrow A + X^+
\]

In these equations $A$ and $X$ denote heavy particles whereas $p$, $q$, $r$ and $s$ denote principal quantum numbers. The charge transfer balance is not electron temperature dependent and therefore levels populated by CT show no response to electron cooling. The excitation transfer balance is only indirectly dependent on the electron temperature since the populations of levels $p$, $q$, $r$ and $s$ are electron temperature dependent.

In Fig. 4 a typical response to power interruption of a level with a Saha-like behavior is plotted [12]. Measurements are performed with a 100 MHz argon ICP operated at 1.3 kW [11]. After the Saha-jump (line “1” in Fig. 4) the emission decays due to electron recombination and diffusion with a typical decay time of $\tau_{\text{decay}} = 150$ μs (“2”). Af-
It should be noted, that in general several mechanisms will contribute to the population of a certain level and that a Saha-like response by no means indicates that the Saha-balance is the only population mechanism. The response in Fig. 4 is called Saha-like since the behavior of the line intensity during power interruption, especially the upward jump as a response to electron cooling, shows that the Saha-balance is contributing to the population of the 4p level of argon.

In most plasmas low lying levels respond Boltzmann-like and higher levels respond Saha-like to power interruption. It can be expected that after introducing aqueous analytes or molecular gases into the plasma also high lying levels will shift to a Boltzmann-like response.

The setup used for power interruption experiments is given in Fig. 5. With a computer (PC) both the microwave generator and a multi-channel scaler (MCS) can be controlled. The plasma radiation is focused on the entrance slit of a monochromator where an emission line is selected. The photomultiplier signal is amplified and filtered in order to enable photon counting. For photon counting a multi-channel scaler (MCS) has been used which has 4096 channels and a minimum integration time of 2 μs per channel (cf. Table 1). When the highest resolution is used, the MCS can monitor approximately 8.2 ms continuously. Measurements are started typically 70 μs before the power interruption and since in 2 μs only a few photons are counted, measurements have been averaged 5000 times in order to reduce the noise level.

3.2 Experimental results

In Fig. 6 a typical response of an argon line (4p-4s) from a TIA plasma is given. The Saha-like response of the line intensity to electron cooling after power-removal (the upward jump) and the very fast decay of the emission afterwards should be noted. The decay time of the intensity equals $\tau_{\text{decay}} \approx 2.4 \mu s$. In reality this decay time might be even smaller since the resolution of the multi-channel scaler is 2 μs. It should be realized that the decay time of the generator (i.e. the time elapsed between “power off” and reaching 10% of the original power) is 1-2 μs and will largely contribute to the observed emission decay time. For measurements with a better time resolution, therefore both the MCS and the generator should be changed. As already

![Fig. 4: A typical Saha-like response of an argon line (7s-4p) to power interruption as obtained from a 100 MHz ICP.](image)

![Fig. 5: Set-up used for power interruption experiments. The microwave generator and the multi-channel scaler (MCS) are computer-controlled. The photomultiplier signal is amplified and discriminated before photon counting (cf. Table 1).](image)

![Fig. 6: Typical response of an argon line (4p-4s at 811.5 nm) to power interruption in a plasma created by the TIA (left). From the delayed response the axial gas velocity can be determined as a function of the height above the nozzle (AN). An example is depicted on the right](image)
shown, the electron density decay in an ICP is much slower, typically $\tau_{\text{decay}} \approx 150 \mu$s, cf. Fig. 4. This is largely due to the significantly larger radial dimensions of the ICP. Therefore diffusion losses are slower than for TIA plasmas. In Fig. 6 an instantaneous sharp increase of the argon line intensity can be observed after “power on”. This Boltzmann-like jump is totally different than the Saha-like heating jump which is observed for the ICP (cf. Fig. 4). The explanation for this difference is that the electron density for the TIA has dropped towards a negligible level during “power off” and that therefore the plasma has to be reignited again (which is a process dominated by electron excitation and therefore Boltzmann-like), whereas for the ICP the electron density is still significantly high and ionization processes are important when the power is switched on again.

The instantaneous responses after “power on” or “power off” should be distinguished from the so-called delayed response, which probably is caused by the propagation of a local disturbance of the electron density in the ionizing part of the plasma. This delayed response is “frozen” in the plasma and is transported downstream with the gas velocity. From the time of arrival at different heights in the plasma consequently the local axial gas velocity can be determined, cf. Fig. 6 on the right. Obtained values (approximately 22 m·s⁻¹) are slightly higher than typical values for the ICP (approximately 14 m·s⁻¹ [13]). A limitation of this method for determining the gas velocity however, is that more downstream in the plasma the intensity of the delayed response becomes weaker and the peak becomes broader. Therefore it becomes difficult to locate its maximum exactly.

In Fig. 7 the relative height of the Saha-jump (scaled to the line intensity during normal “steady state” operation) is depicted for several species as a function of the amount of CO₂ added to the argon discharge. It should be noted that this height is unity the response to power interruption is Boltzmann-like populated by electron excitation. Line intensities of levels of species which have high excitation energies and which are relatively close to the ionization potential (e.g. levels Ar and O) show a much higher Saha-jump, at least when no additional CO₂ is added. After the addition of CO₂ the height of the Saha-jump rapidly decreases and even if only 0.5% of the plasma gas is carbon dioxide, the Saha-jump has already vanished completely and the response to power interruption becomes fully Boltzmann-like. Since recombination processes are proportional to $n_e^2$ while excitation processes are proportional to $n_e$ this might indicate that the electron density is significantly decreased after molecular gas injection. A possible extra loss channel for electrons is dissociative recombination.

The height of the Saha-jump can provide information about the ratio $T_e/T_h$ (although this information is not very accurate since the electrons do not completely cool down towards the heavy particle temperature during “power off”). However, unlike for measurements performed on an ICP [13], in TIA plasmas the duration of the Saha-jump is too short compared to the resolution of the MCS and the decay time of the generator to determine the height of the jump with satisfactory accuracy. Therefore the presented measurements cannot be used to determine this temperature ratio.

In Fig. 8 the response of an analyte (Na, 3p-3s at 589.00 nm) is given at different heights in the plasma. Just above the nozzle the response is Boltzmann-like and a fast decay of the emission can be observed after removing the microwave power. This is in agreement with the behavior of other line intensities of elements which have rather low excitation energies as well.

However, in the recombination zone, downstream in the after-glow of the plasma, where the analyte emission is still rather strong, no response to power emission can be observed. During steady-state conditions the electron density and temperature at these heights are already much lower than just above the nozzle [7]. Therefore it is very unlikely that in the recombination zone the analyte is still dominantly excited by electron ruled processes. This is con-
firmed by the power interruption experiments since the analyte shows no response to electron cooling. Since radiative levels are not populated by excitation mechanisms which are dependent on the electron temperature or density, electron impact, recombination or charge transfer can be ruled out.

A possible mechanism is excitation transfer from a metastable (cf. Eq. 6). Also Penning ionization by a metastable should not be ruled out:

\[ X^m + Y \rightarrow X + Y^+ + e^- , \]

where \( X^m \) denotes a metastable, \( Y \) the analyte and \( Y^+ \) the corresponding excited analyte ion. Recombination of sodium ions can create excited sodium atoms and consequently emission. Metastables can be present in the plasma from the argon carrier gas (the 4s levels at 11.55 and 11.72 eV) or nitrogen introduced from the ambient air (molecular nitrogen \( N_2(A) \) at 6.18 eV or atomic nitrogen: \( N(^2D) \) and \( N(^2P) \) at 2.38 and 3.57 eV, respectively). Since the excitation energy of the observed sodium line is 2.10 eV only, the internal energy of all given metastables is sufficient for the analyte excitation. Due to this relatively low excitation energy, even thermal excitation by heavy particles cannot be ruled out completely. However, since the heavy particle temperature at 28 mm above the nozzle is approximately 0.3 eV [10], thermal excitation is not very likely. Measurements with analytes having different excitation and ionization energies could provide more information about the exact excitation mechanisms.

4 Discussion and conclusions

From measurements performed on microwave induced plasmas produced by the TIA (torche à injection axiale) we have found that the introduction of molecular species has a strong impact on argon plasmas: The emission spectrum is dominated by molecular bands of diatomic dissociation and association products and changes in excitation mechanisms are observed after the introduction of molecular species.

It is found that the plasmas are strongly influenced by the ambient gas. If the plasma is expanding into the air, strong emission bands of molecules containing nitrogen atoms (NH, CN) are observed. If the plasma is expanding into an argon environment, the influence of an additional air flow on the analytical power is similar to the influence of the analytical power of the inductively coupled plasma (ICP). A major difference, however, is that the TIA can withstand much higher molecular gas flows before the analytical performance is severely affected.

Information about the excitation mechanisms has been obtained by studying the time-dependent intensities of atomic lines or molecular bands during power interruption. It is found that after the introduction of small amounts of molecular gases into argon discharges (i.e. more than 0.5% of \( CO_2 \) compared to the argon carrier gas) the response of line intensities to power interruption already becomes Boltzmann-like for all species, even for the argon lines. In argon discharges without molecular gas or aerosol introduction, on the other hand, the response to power interruption of these argon lines is clearly Saha-like.

Remarkable differences have been found between the ionizing part of the plasma (i.e. just above the nozzle) and the recombination zone of the plasma (in the after-glow). Whereas just above the nozzle the response of a sodium emission line shows a Boltzmann-like response to power interruption, no response at all can be observed in the recombination zone. This shows that in this region the analyte is not excited by a mechanism ruled by electrons. When thermal excitation by heavy particles is neglected, the only mechanisms which seem possible are excitation transfer from a metastable or Penning ionization by a metastable. Experiments with other elements will be done in near future to investigate the involvement of the metastable 4s levels of argon (\( E_{exc} = 11.55 \) and 11.72 eV).

References