

JAAS

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Enhancement of Analyte Atomic Lines with Excitation Energies of about 5 eV in the Presence of Molecular Gases in Analytical Glow Discharges

Sohail Mushtaq^a, Edward B.M. Steers^a, Juliet C. Pickering^b, and Petr Šmid^c

kwikCite this: DOI:
10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Small amounts of hydrogen or oxygen in either argon or neon plasmas cause unexplained enhanced excitation of various analyte atomic lines with upper energies close to 5 eV. We suggest this enhancement is due to three body collisions involving two hydrogen or oxygen atoms and a sample atom.

In recent years, it has been observed that there is some enhanced excitation of various analyte atomic spectral lines, particularly in the 5 eV range, in the presence of molecular gases (oxygen or hydrogen) in analytical glow discharges. A number of studies have been made on the effects of known amounts of molecular gases (hydrogen, nitrogen and oxygen) in the plasma gas on the discharge parameters and emitted spectra, using commercial glow discharge optical emission spectrometry (GD-OES) equipment. Until recently, such systems used polychromators and could only produce data on a very few preselected spectral lines for each element. Initially Fischer *et al.*¹ studied the effects of oxygen and nitrogen. Later, Bengtson and Hånström² clearly demonstrated the effects of hydrogen on analyte spectral lines. They showed that the intensities of the Cr I 305.4 nm and Si I 288.2 nm lines, which both have excitation energies in the 5 eV range, increase strongly in the presence of hydrogen. Further investigations have been carried out by Fernández *et al.*³ on the effects of hydrogen, nitrogen and oxygen and more work on the effects of hydrogen has been reported by Martin *et al.*⁴ Such studies on a few selected spectral lines can produce valuable information for analytical use, but to understand the discharge processes producing these effects, the way in which the changes depend on the energy of the upper state of the transition must be known and for this it is necessary to record the intensity changes of a large number of lines of a given element.

Hodoroaba *et al.*⁵ carried out a detailed study of the effect of hydrogen on the intensity of a large number of copper lines and observed that the intensity of Cu I lines tended to increase. For this

work, a scanning spectrometer was used; a particular line was selected, and its intensity measured for a series of gas mixtures, before the next line was selected and the process repeated. This was a tedious method and liable to error, if mixtures were not reproduced exactly. Thus the major difference in the plots for the 324.754 nm and 327.396 nm lines is due to experimental error.⁶ Hodoroaba *et al.*⁷ also used a commercial GDS system to measure the effect of added hydrogen on one or two lines of a number of other elements.

For many years after photographic spectroscopy became rare, the only spectrometers capable of recording a large number of spectral lines simultaneously were high resolution Fourier transform spectrometers (FTS). Šmid *et al.*⁸ used the Imperial College high resolution vis-uv FTS⁹ to carry out the first investigation of the effect of added nitrogen on the intensities of a large number of spectral lines of iron and titanium in an argon plasma and subsequently carried out similar experiments with added hydrogen, recording lines in the region 200-600 nm. This instrument has a chromatic resolving power of up to 2×10^6 at 200 nm, so it is possible to separate close lines and to observe line structure and self absorption.⁸ In 2008, Šmid *et al.* reported that the intensities of several iron atomic emission lines with excitation energy between 5.3 and 5.6 eV were strongly enhanced in the presence of hydrogen.¹⁰ On the other hand, it was found that nitrogen did not produce any similar effects. By this time, commercial GDS instruments using CCD arrays to record spectral lines had become available for multi-line investigations (but with much lower resolving power, so separation of close lying lines is not possible) and data obtained using the LECO GDS500A instrument¹¹ was used to supplement the FTS data.

Within the EC GLADNET RTN Mushtaq used the Imperial College FTS to investigate, over a wide spectral range including many spectral lines, the effect of oxygen as an impurity (0.02-0.2% v/v) in analytical GD in argon or neon discharges with various analyte

materials. Mushtaq *et al.*¹² reported enhanced excitation of iron atomic lines with upper levels in the 5 eV energy region with added oxygen in argon GD and a similar effect has been observed with neon as the discharge gas. This study has been extended to other elements, including manganese, copper and titanium. The fact that similar effects occur for argon and neon imply that the effect is not linked with the critical energies of these gases, whereas its occurrence with oxygen and hydrogen but not with nitrogen suggests it is linked with some property of these gases. Requests at various international conferences and scientific meetings for suggestions of the possible cause have not produced any response. This paper shows that it is likely to be linked to a three body collision between two oxygen or hydrogen atoms and a sample atom.

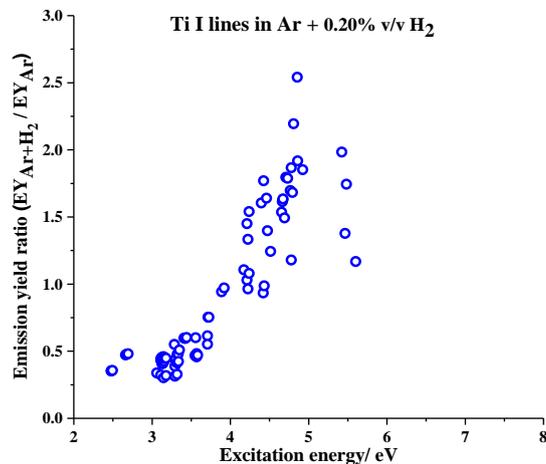


Fig. 1 Emission yield (EY) ratios of observed titanium atomic lines as a function of excitation energy for 0.2% v/v H₂ in argon mixture for 700 V and 20 mA. (EY = Intensity/sputter rate x concentration of the element in the sample, and is used as the Ti line intensities all decrease with added H₂ due to reduced sputter rate)

For a titanium sample in an argon/hydrogen plasma, all the titanium lines showed a severe drop in intensity due to significant decrease in sputter rate with the presence of hydrogen in an argon GD. Therefore, emission yield ratios (which compensate for changes in sputter rate) of the observed titanium atomic lines are plotted in Fig. 1 against their excitation energy for 0.2% v/v hydrogen concentration in argon GD. There is a considerable increase in emission yield ratios of Ti I lines with excitation energy near to 5 eV. In Fig. 2, the emission yield ratios of observed copper atomic lines are plotted against their excitation energy for 0.6% v/v oxygen concentration in a neon GD. A noticeable increase in emission yield ratios for copper atomic lines with excitation energy near to 5 eV is observed. The changes in emission yield ratios in neon/oxygen mixtures due to changes in self-absorption, for example for the Cu I 324.754 nm line, and the suppression of Cu I lines at higher energy levels are discussed in detail in a separate paper.¹³ The present communication concentrates on the hitherto unexplained enhancement of analyte atomic lines with excitation energy near to 5 eV in the presence of oxygen or hydrogen.

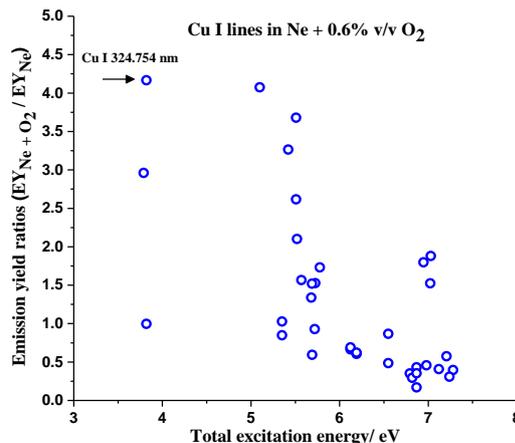
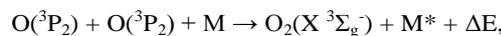
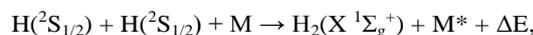


Fig. 2 Emission yield (EY) ratios of observed copper atomic lines as a function of excitation energy for 0.6% v/v O₂ in neon mixture for 700 V and 20 mA.

Following a suggestion from Dr. Hoffmann (IFW Dresden), we now propose a partial explanation for this enhanced excitation. It appears to be due to three body collisional recombination involving two hydrogen or oxygen atoms and a sample atom in its ground or low-lying metastable state, resulting in the formation of a hydrogen or oxygen molecule and the excitation of the sample atom by the recombination energy released by the molecule. There are also likely to be changes in the kinetic energies of the colliding particles, *e.g.*

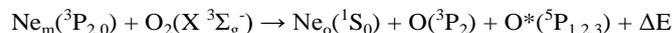


and



where M is the sample atom and the superscript * represents an excited state.

In the case of collisional induced dissociation, the surplus energy ΔE can be carried off by the atoms in the form of kinetic energy and/or direct excitation of one of the resulting particles, for example in neon/oxygen mixtures:



Similarly in the case of the reverse process, three body collisional recombination, which we suggest is occurring here, the excitation of analyte atomic emission lines may occur for a selective range of energies.

The recombination energies of oxygen and hydrogen are 5.15 eV and 4.52 eV respectively, and the excess energy required for the excitation of the sample atoms in some cases can be supplied by the kinetic energy of the colliding particles or by excitation of the sample atoms from low lying metastable levels. On the other hand, the recombination energy of nitrogen is 9.97 eV so any similar effect could only occur at much higher energies above the ionization energy of typical sample atoms. The majority of molecular recombination will take place at the walls of the source, so this process will not be a significant contribution to the recombination rate.¹⁴ However, three body collisional recombination within the gaseous volume

can make a significant contribution to the population of particular excited levels of sample atoms.¹⁵ The factors which affect the magnitude of the enhancement are discussed below. The process is probably dependent on the discharge current, gas pressure and temperature, and most importantly on the availability of atomic states of the sputtered atoms with the appropriate excitation energy.

The intensity ratios (line intensity using argon – molecular gas mixture / intensity using argon) of observed sample atomic lines as a function of their excitation energy for various hydrogen concentrations are shown in Fig. 3, for manganese, iron and copper samples. The intensity ratios of lines with excitation energy near to 5 eV increase significantly with the increase of hydrogen concentration in argon plasmas. At low hydrogen concentration (0.05% v/v), the enhancement near to 5 eV cannot be clearly identified. However, at higher hydrogen concentrations the enhancement of the intensity ratios becomes more significant. In general, hydrogen in an argon plasma reduces the sputter rate of analyte materials; however, Fig. 3 shows that even without including sputter rate changes in this case (*i.e.* intensity ratios, not emission yield ratios), the excited populations in the 5 eV energy range increase significantly with the increase of hydrogen.

In Fig. 4(a), the changes in iron atomic line intensities as a function of their excitation energy in Ar/H₂ mixtures for different currents are shown. Similar studies have been carried out on iron atomic lines in Ar/O₂ mixtures for two different currents and results are presented in Fig. 4(b). It is quite clear in Fig. 4(a), when Ar/H₂ mixtures are used for two different currents, the enhancement of Fe I lines due to a three body collisional recombination process is more pronounced when lower currents are used. As discussed above, the enhancement for various analyte atomic lines is more pronounced at higher H₂ or O₂ concentrations. However, under these conditions the sputter rate for some analytes decreases very significantly in Ar/O₂ plasmas, much more than those with Ar/H₂ mixtures,¹² hence the overall intensity falls and in some cases (at 700 V and 10 mA) many analyte atomic lines cannot be observed in Ar/O₂ mixtures. Therefore, for an iron sample with Ar/O₂ mixtures, intensity ratios are shown for currents of 20 and 40 mA. Even then, the effect of the added oxygen is an overall fall in intensities. It can be observed that the selective enhancement, though less than with hydrogen, is again more pronounced when lower currents are used. The effect of current was shown by Steers *et al.*,¹⁶ where changes in titanium atomic line intensities as a function of their excitation energy for various currents are reported. As the current is increased, the number density of sputtered atoms increases, whilst that of the molecular gas atoms does not change greatly, so that the selective process has a smaller role in the overall excitation.

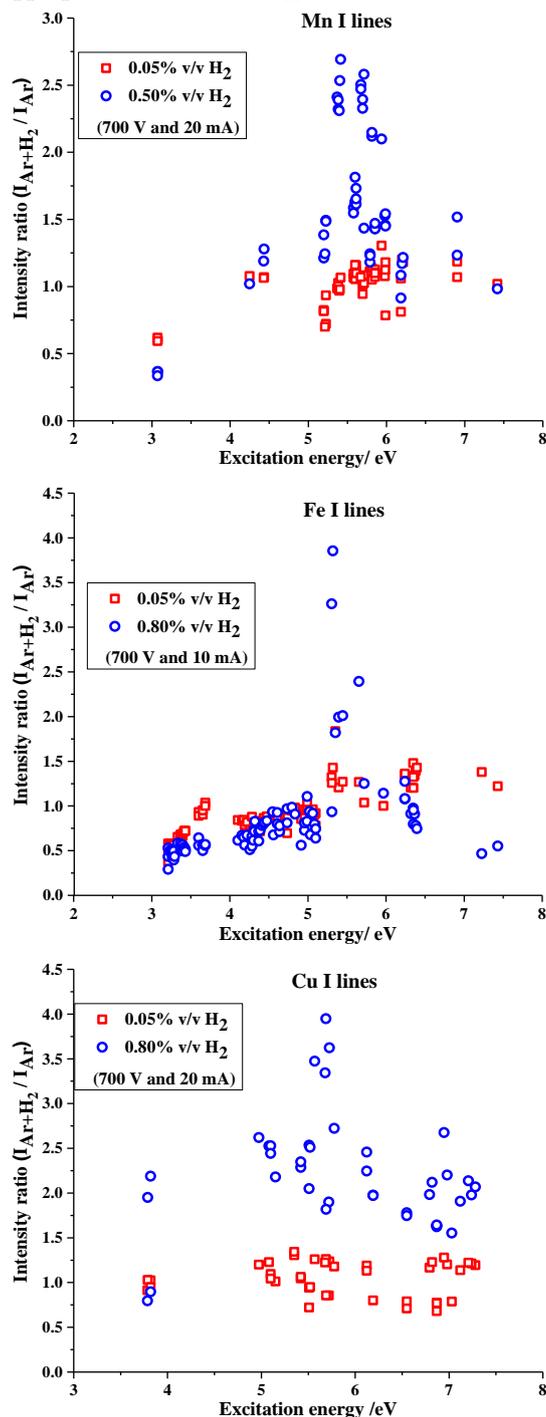


Fig. 3 The intensity ratios of manganese, iron and copper atomic lines as a function of different hydrogen concentrations in argon plasma.

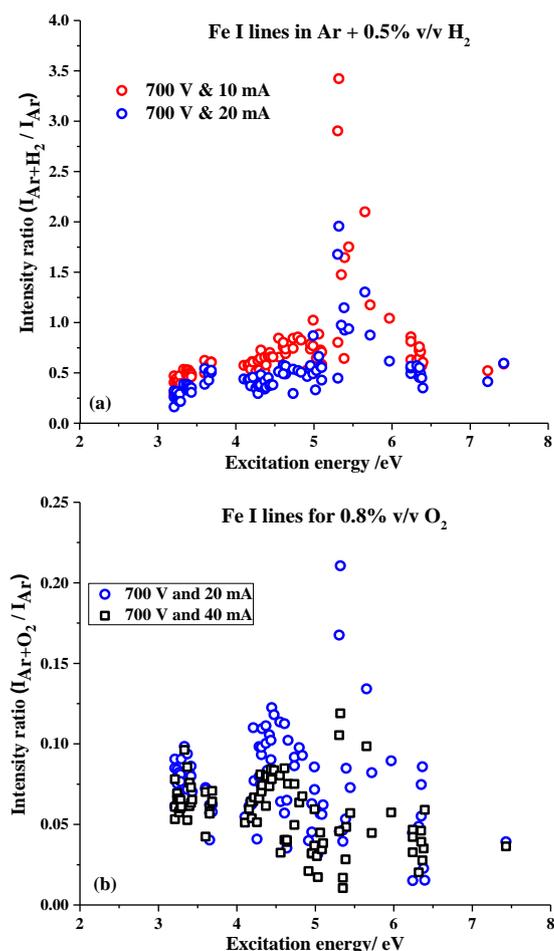


Fig. 4 Ratios of the Fe I line intensities in (a) Ar + 0.5% v/v H₂, 700 V, 10 mA and 20 mA and (b) Ar + 0.8% v/v O₂, 700 V, 20 mA and 40 mA to intensities in pure argon, plotted against excitation energy of upper level.

Some of the measurements using polychromators on the effect of added hydrogen or oxygen on particular lines also show strong enhancement when the energy of the upper level is about 5 eV, though with only one or two lines it is not possible to see the full picture. Thus Bengtson and Hännström² showed that the Cr I 305.388 nm line (upper level 5.089 eV) and the Si I 288.158 nm line (upper level 5.082 eV) were both enhanced in the presence of hydrogen, and Hororoaba *et al.*⁷ confirmed the effect for the silicon line. In other cases, with somewhat greater energies of the upper level, reported enhancements may well be due to the reduction of self absorption.

Conclusions

In many cases in both argon and neon plasmas, there is enhanced excitation of analyte atomic lines with upper energies close to 5 eV in the presence of small amounts of hydrogen or oxygen. To observe this effect fully, it is essential to record spectra over a very wide spectral range, so as to include as many energy levels as possible, otherwise critical values may be overlooked.

We suggest in this communication, that the enhancement is due to three body collisions involving two hydrogen or oxygen atoms and a sample atom resulting in the formation of an H₂ or O₂ molecule and the excitation of the sample atoms by the recombination energy released by the molecule. This effect is more pronounced when higher concentrations of added oxygen or hydrogen in plasma and lower values for discharge currents are used. The amount of hydrogen introduced into a plasma when there is hydrogen contamination is sufficient to cause changes in relative intensities.² On the other hand, effects with oxygen only become significant at higher oxygen concentrations than those that occur when an oxide is sputtered.^{17,18} It is not clear what selection rules, if any, apply for this process, and why very pronounced enhancement of some particular levels occurs for some element/molecular gas combinations, whilst for others the effect seems to be smaller in magnitude and less selective.

Detailed studies of the three body collisional recombination in low pressure glow discharges in presence of oxygen or hydrogen are continuing.

Notes and references

^a London Metropolitan University, 166-220 Holloway Road, London, N7 8DB, UK.

^b Blackett Laboratory, Imperial College, London, SW7 2AZ, UK.

^cNow at: AQura GmbH, Rodenbacher Chaussee 4, D63457 Hanau-Wolfgang, Germany.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

References

- 1 W. Fischer, W. Naoumidis and H. Nickel, "Effects of a controlled addition of nitrogen and oxygen to argon on the analytical parameters of glow discharge optical emission spectrometry", *J. Anal. At. Spectrom.*, 1994, **9**, 375-380.
- 2 A. Bengtson and S. Hännström, "The influence of hydrogen on emission intensities in GD-OES consequences for quantitative depth profile analysis", *Proceed. of 5th Int. Conf. On Prog. In Anal. Chem. in Steel & Metal Ind.*, 1999, 47-54.
- 3 B. Fernández, N. Bordel, C. Pérez, R. Pereiro and A. Sanz-Medel, "The influence of hydrogen, nitrogen or oxygen additions to radiofrequency argon glow discharges for optical emission spectrometry", *J. Anal. At. Spectrom.*, 2002, **17**, 1549-1555.
- 4 A. Martin, R. Pereiro, N. Bordel, and A. San-Medel, "Hydrogen effects on copper, zinc and nickel atomic emission lines in argon radiofrequency glow discharge optical emission spectrometry", *Spectrochim. Acta Part B*, 2008, **63**, 692-699.
- 5 V-D. Hodoroaba, V. Hoffmann, E.B.M. Steers, and K. Wetzig, "Emission spectra of copper and argon in an argon glow discharge containing small quantities of hydrogen", *J. Anal. At. Spectrom.*, 2000, **15**, 951-958.

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
- 6 V. Weinstein, Ph. D. Thesis, London Metropolitan University, 2011.
 - 7 V-D. Hodoroaba, V. Hoffmann, E. B.M. Steers, and K. Wetzig, "Investigations of the effect of hydrogen in an argon glow discharge", *J. Anal. At. Spectrom.*, 2000, **15**, 1075-1080.
 - 8 P. Šmid, E. B.M. Steers, Z. Weiss and J. Vlcek, "The effect of nitrogen on analytical glow discharges studied by high resolution Fourier transform spectroscopy", *J. Anal. At. Spectrom.*, 2003, **18**, 549-556.
 - 9 J. C. Pickering, "High resolution Fourier transform spectroscopy with the Imperial College UV-FT spectrometer and its applications to astrophysics and atmospheric physics", *Vib. Spec.*, 2002, **29**, 27-43.
 - 10 P. Šmid, E. B.M. Steers, Z. Weiss, J. C. Pickering and V. Hoffmann, "The effect of hydrogen and nitrogen on emission spectra of iron and titanium atomic lines in analytical glow discharges" *J. Anal. At. Spectrom.*, 2008, **23**, 1223-1233.
 - 11 K. Marshall and P. M. Willis, Centered Sphere Spectrometer, US Patent 6023330.
 - 12 S. Mushtaq, E. B.M. Steers, J. C. Pickering, T. Gusarova, P. Šmid, and V. Weinstein, "Effects of traces of oxygen on Grimm-type glow discharges in argon", *J. Anal. At. Spectrom.*, 2011, **26**, 766-775.
 - 13 S. Mushtaq, E. B.M. Steers, J. C. Pickering and V. Weinstein, "Effect of small quantities of oxygen in a neon glow discharge", *submitted, J. Anal. At. Spectrom.*, 2014, IGDSS special issue.
 - 14 A. Bogaerts and R. Gijbels, "Effects of small amounts of hydrogen added to argon glow discharges: Hybrid Monte Carlo-fluid model" *Phys. Rev. E.*, 2002, **65**, 056402-15.
 - 15 A. Bogaerts, *Private Communication*.
 - 16 E. B.M. Steers, P. Šmid, V. Hoffmann and Z. Weiss, "The effects of traces of molecular gases (H₂, N₂, & O₂) in glow discharges in noble gases" *J. Phys., Conf. Ser.*, 2008, **133**, 012020-
 - 17 S. Mushtaq, J. C. Pickering, E. B.M. Steers, P. Horvath, J. A. Whitby and J. Michler, "The role of oxygen in analytical glow discharges: GD-OES and GD-ToF-MS studies" *J. Anal. At. Spectrom.*, 2011, **26**, 1746-1755.
 - 18 S. Mushtaq, V. Hoffmann, E. B.M. Steers and J. C. Pickering, "Comparison of a sample containing oxide with a pure sample with argon-oxygen mixture" *J. Anal. At. Spectrom.*, 2012, **27**, 1423-1431.