SELEKTIVE ANREGUNG IN DER GLIMMENTLANDUNG – IST DAS IN DER PRAKTISCHEN ELEMENTARANALYSE WICHTIG?

E.B.M. Steers, S. Mushtaq

London Metropolitan University,
166-220 Holloway Road, London, N7 8DB, UK
e.steers@londonmet.ac.uk

Gladnet Work Package 2 – Effect of added molecular gases on fundamental processes:

Dr Petr Smid, ER LondonMet, (AQura)

Viktoria Weinstein, ESR LondonMet

Sohail Mushtaq, ESR, Imperial College
(Postdoc. Fellow, London Metropolitan University.)

Many thanks to these colleagues, to Dr Juliet Pickering for the use of the Imperial College VUV Fourier Transform spectrometer, to the EC for the Gladnet RTN, 2007-2011, (Contract No. MRTN-CT-2006-035459 and to Dr Volker Hoffmann and Dr Zdenek Weiss for experimental assistance and helpful discussions.

Excitation and Ionisation Processes

Electronic excitation (EE) and **ionisation (EI)**:

Collisions with metastable atoms – **Penning Ionisation (PI)** and **Penning Excitation (PE)**

PI: $A_o + B_m \Rightarrow A_o^+ + B_o + e + \Delta E$

or $A_o + B_m \Rightarrow A^{+*} + B_o + e + \Delta E$,

PE: $A_o + B_m \Rightarrow A^* + B_o + \Delta E$

Collisions with ions – charge transfer

Symmetric Charge Transfer: $A^+ + A \Rightarrow A + A^+$

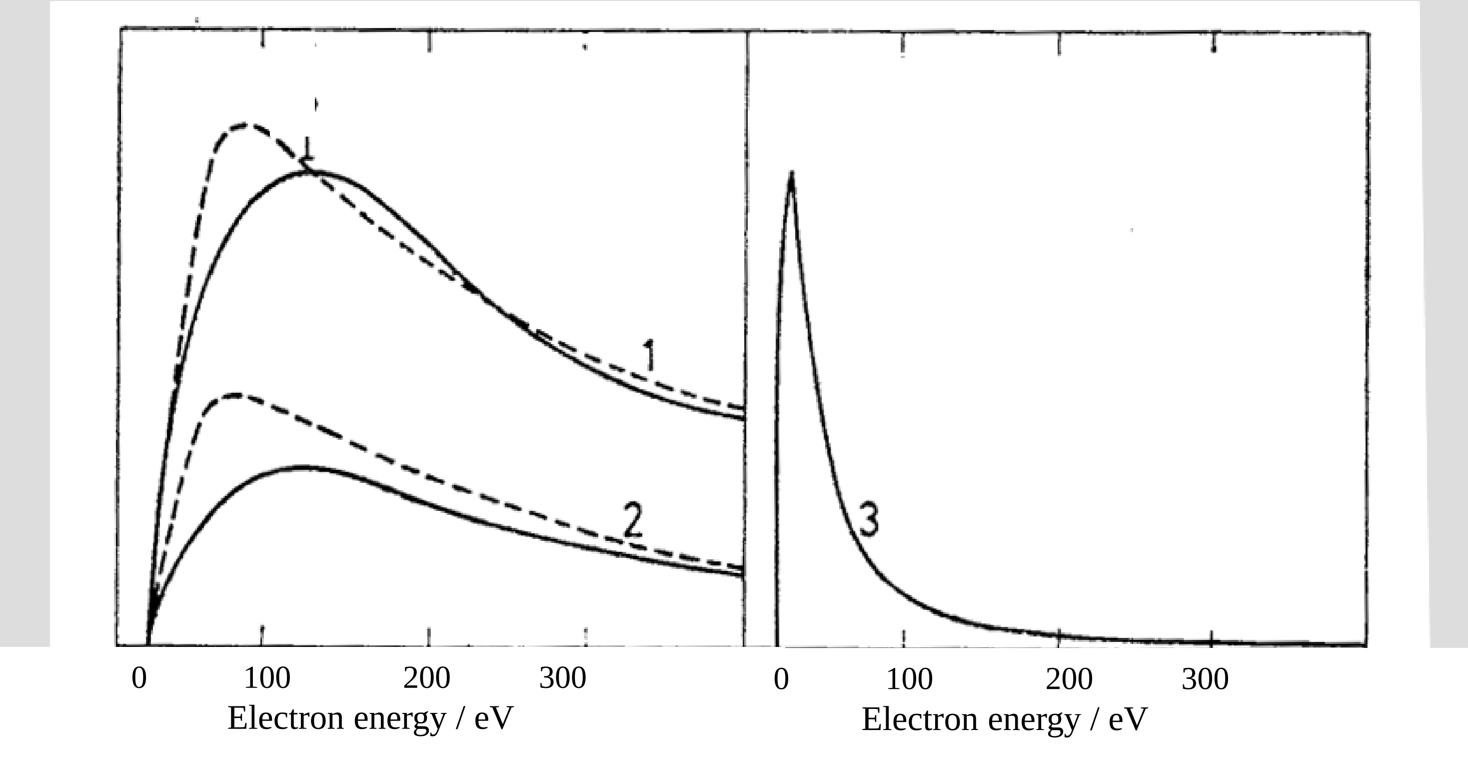
Asymmetric Charge Transfer (ACT): $A^+ + B \Rightarrow A + B^{+*} + \Delta E$

Collisions with high energy ions and atoms

Radiative decay from higher energy levels (‘cascade’)

Electronic excitation (EE) and **ionisation (EI)**:

Excitation functions for some He I lines



Curve	Wavelength /nm	Upper level	Lower level
1	501.567	$3p\ ^1P_1$	$2s\ ^1S_0$
2	396.473	$4p\ ^1P_1$	$2s\ ^1S_0$
3	388.865	$3p\ ^3P_{2,1,0}$	$2s\ ^3S_1$

Ground State $1s^2\ ^1S_0$

Dotted curve – calculated

Full curve = experimental

Collisions with metastable atoms

Penning Ionisation (PI)

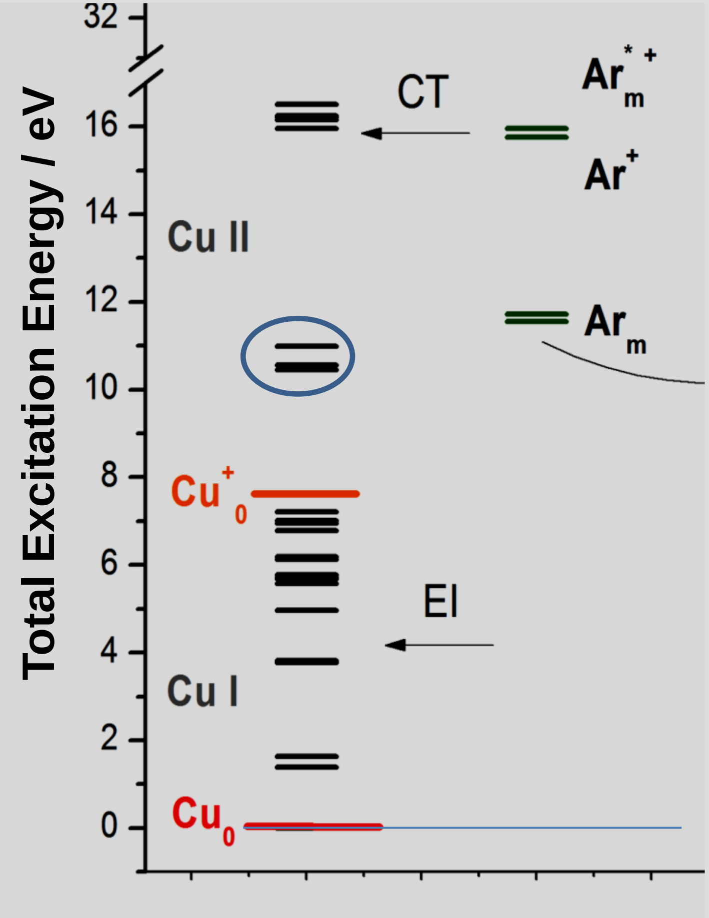
Penning Excitation (PE)

PI: $A_o + B_m \Rightarrow A_o^+ + B_o + e + \Delta E$
or $A_o + B_m \Rightarrow A^{+*} + B_o + e + \Delta E$
ΔE positive, but need not be small; non-resonant reaction

PE: $A_o + B_m \Rightarrow A^* + B_o + \Delta E$
ΔE small; energy resonance needed

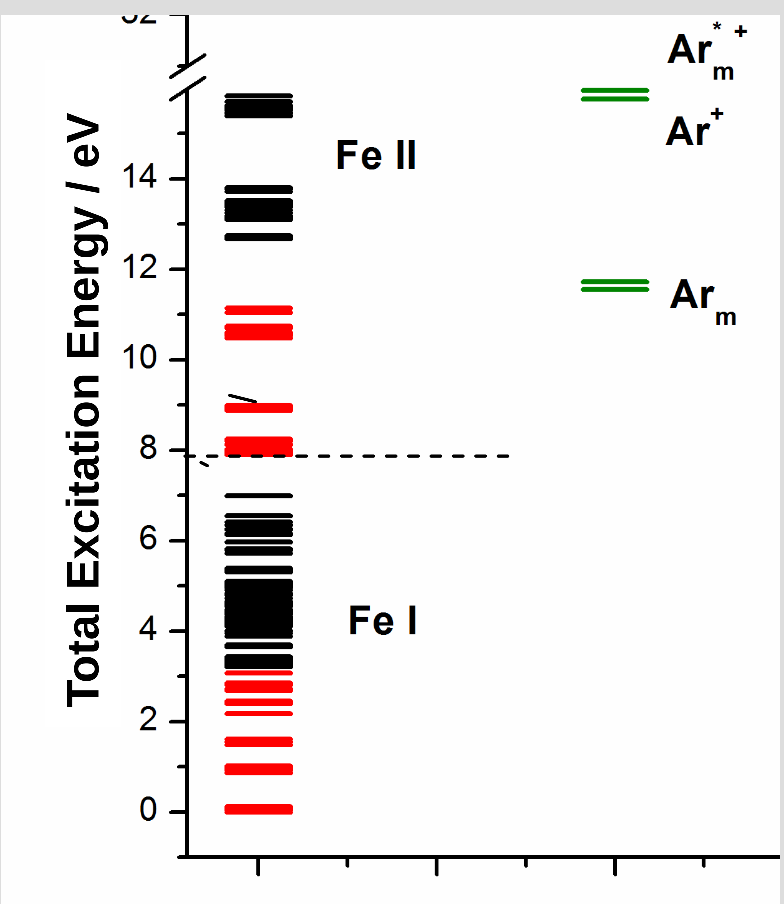
A & B can be ATOMS or IONS

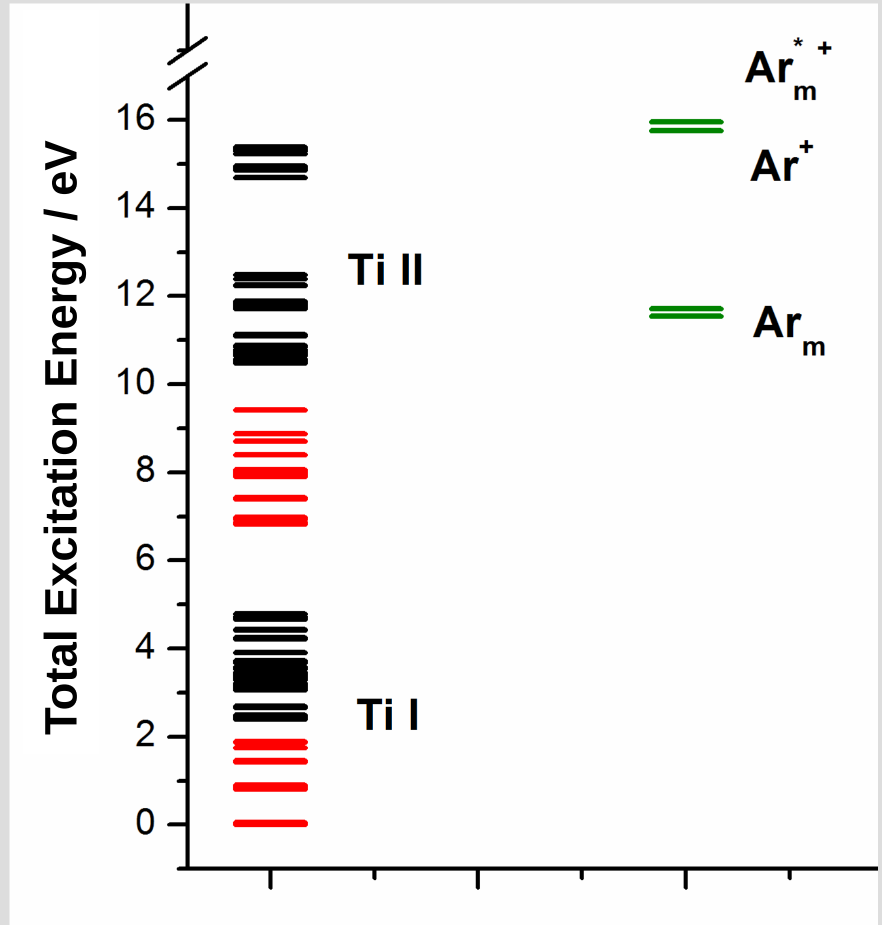
Copper – ions produced by PI either in ground state or in a metastable state



LONDON metropolitan university

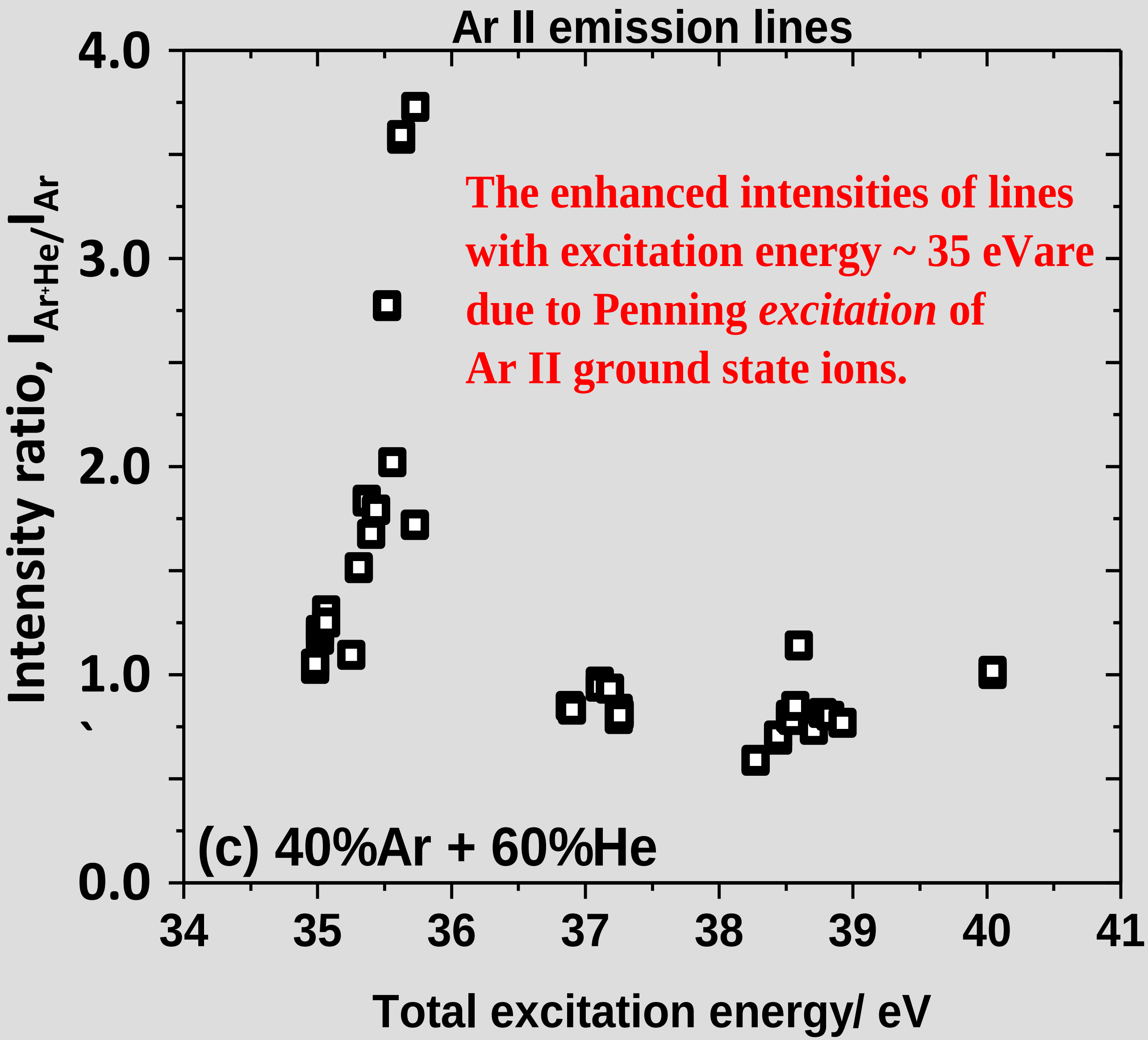
Penning Ionisation (contd)





For Fe II, no transitions observed from levels excited by Penning Ionisation; levels in RED are metastable

Penning Excitation : $A_o + B_m \Rightarrow A^* + B_o + \Delta E$



Collisions with ions – charge transfer

Symmetric Charge Transfer:

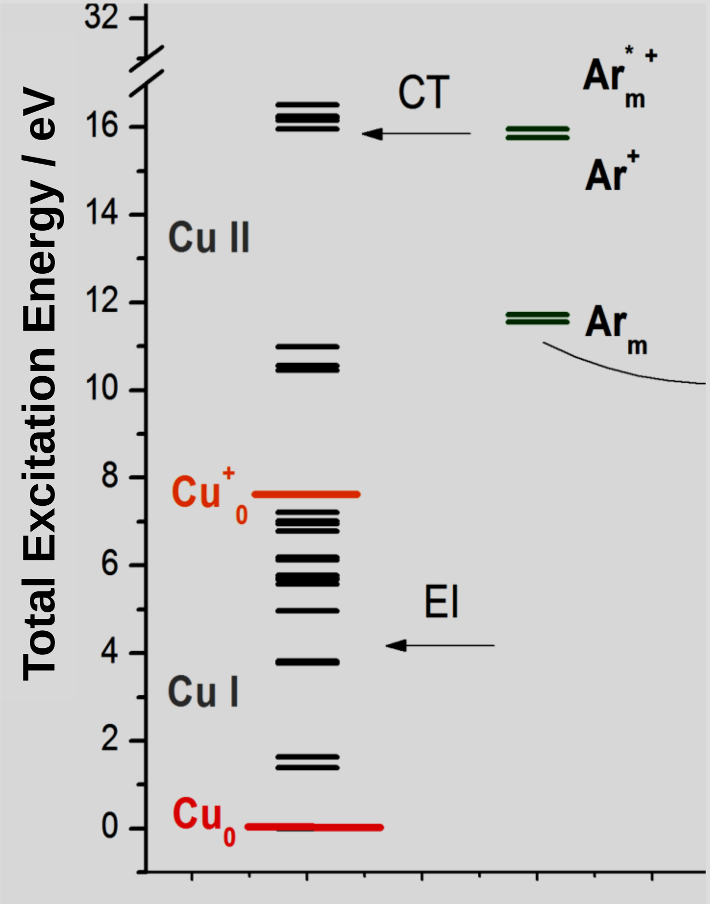
$A^+ + A \Rightarrow A + A^+$

Momentum of particles unchanged

Asymmetric Charge Transfer (ACT):
$A^+ + B \Rightarrow A + B^{+*} + \Delta E$

ΔE must be small,
normally positive (exothermal), can be negative (endothermal).
Resonant reaction

Ionisation energies – O 13.617 eV,
Kr 13.999 eV



Partial energy level diagram for Cu

ARGON with added Hydrogen. Copper sample

Hodoroaba: 2.5 mm diam. anode tube, fixed voltage and pressure. Intensities recorded by setting on one line with monochromator, varying the H_2 concentration. Current falls when hydrogen is added.

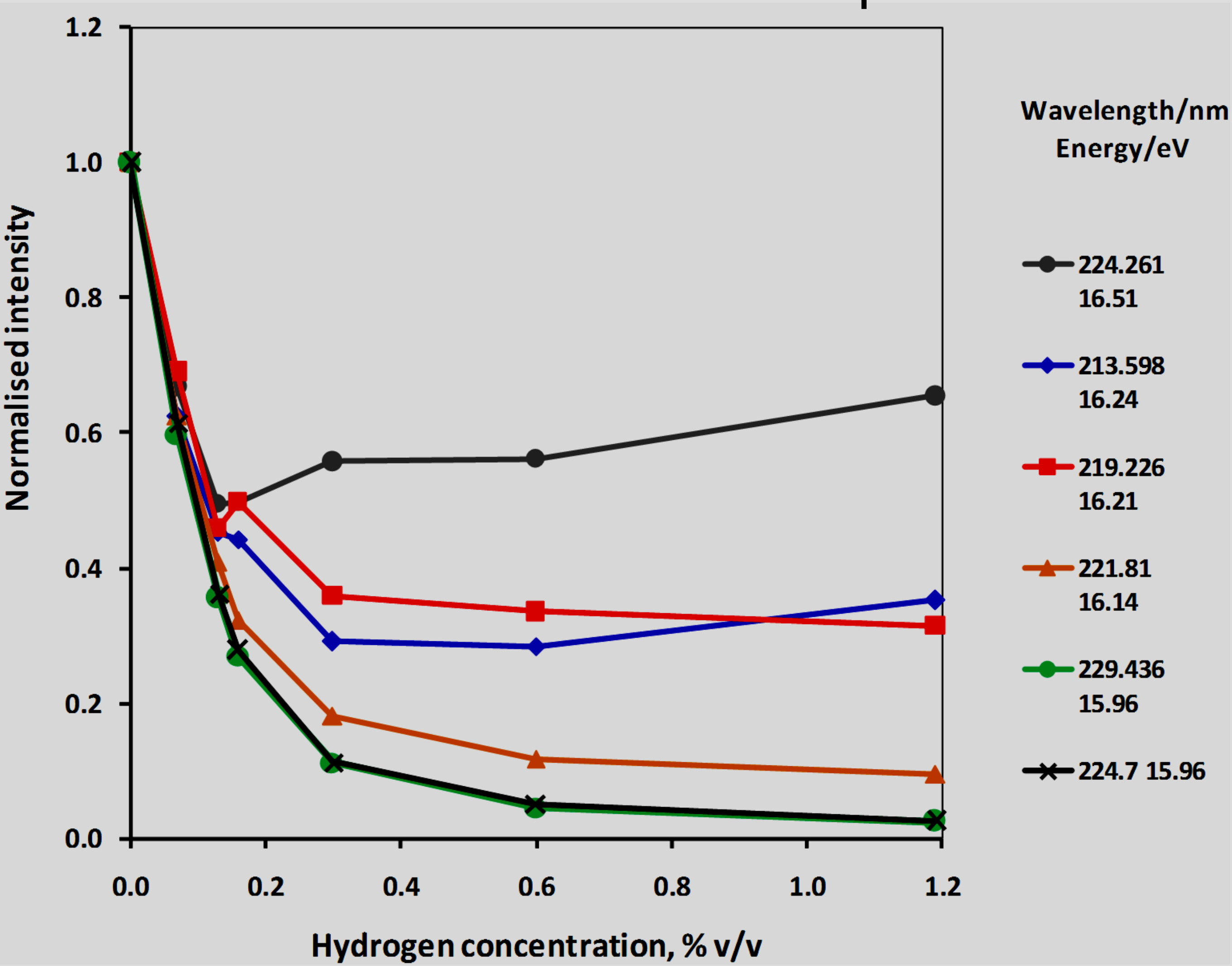
Weinstein: Spectrum recorded over very wide ranges - e.g 200-300 and 300-600 nm - with FT spectrometer; then to next H_2 concentration.

A. 2.5.mm anode tube, fixed voltage and pressure. Very similar trends to those observed by Hodoroaba.
B. 4 mm anode tube, fixed voltage (700 V), current (20 mA), pressure must be increased when H_2 added. Same trends as Hodoroaba, but magnitude different.

Effect produced by hydrogen depends on discharge conditions

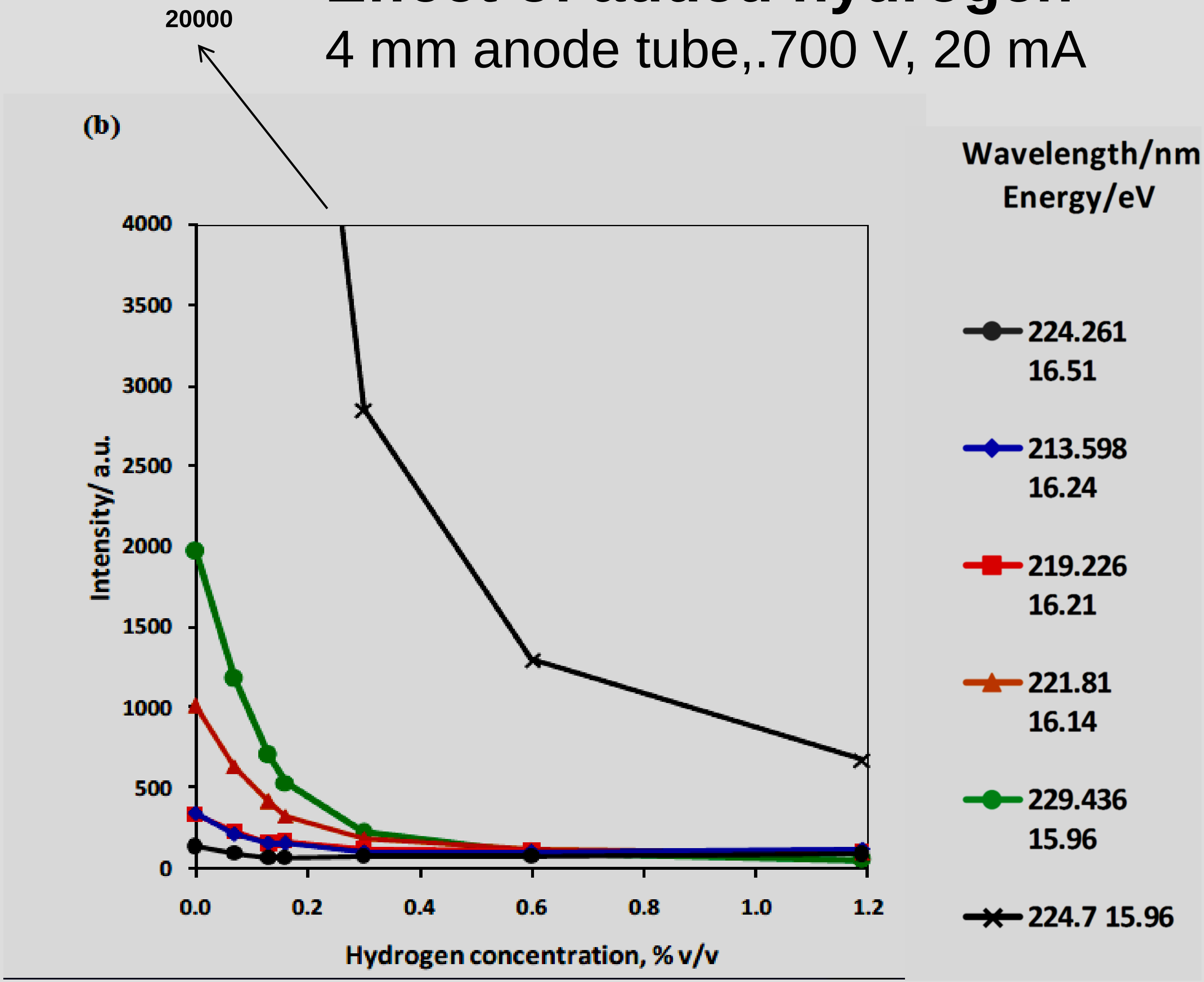
Effect of added hydrogen (contd)

Intensities normalised to 1 in pure Ar

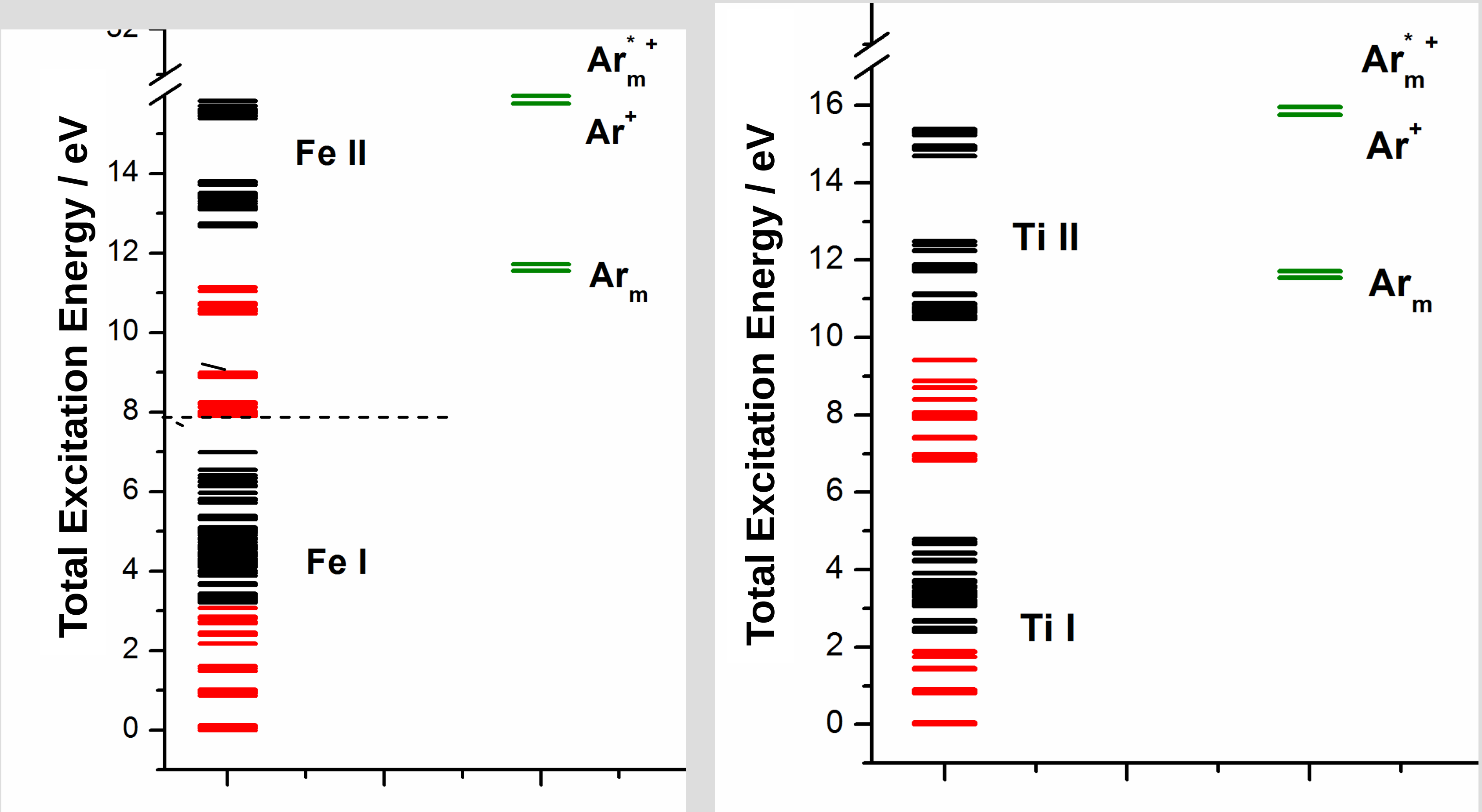


Effect of added hydrogen

4 mm anode tube,.700 V, 20 mA

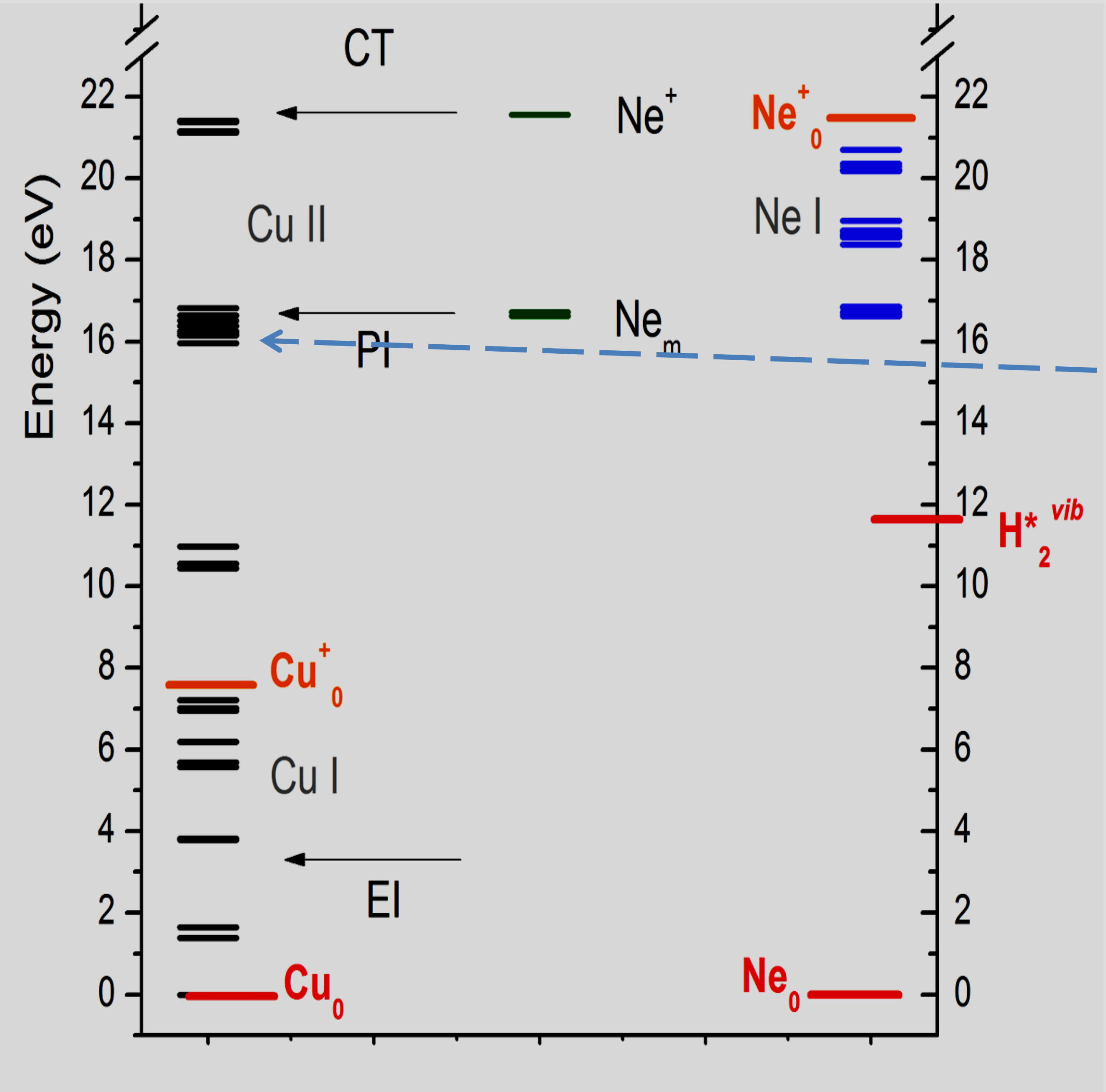


Argon Asymmetric Charge Transfer



Ar-ACT possible for both Fe and Ti

Neon / Copper discharges



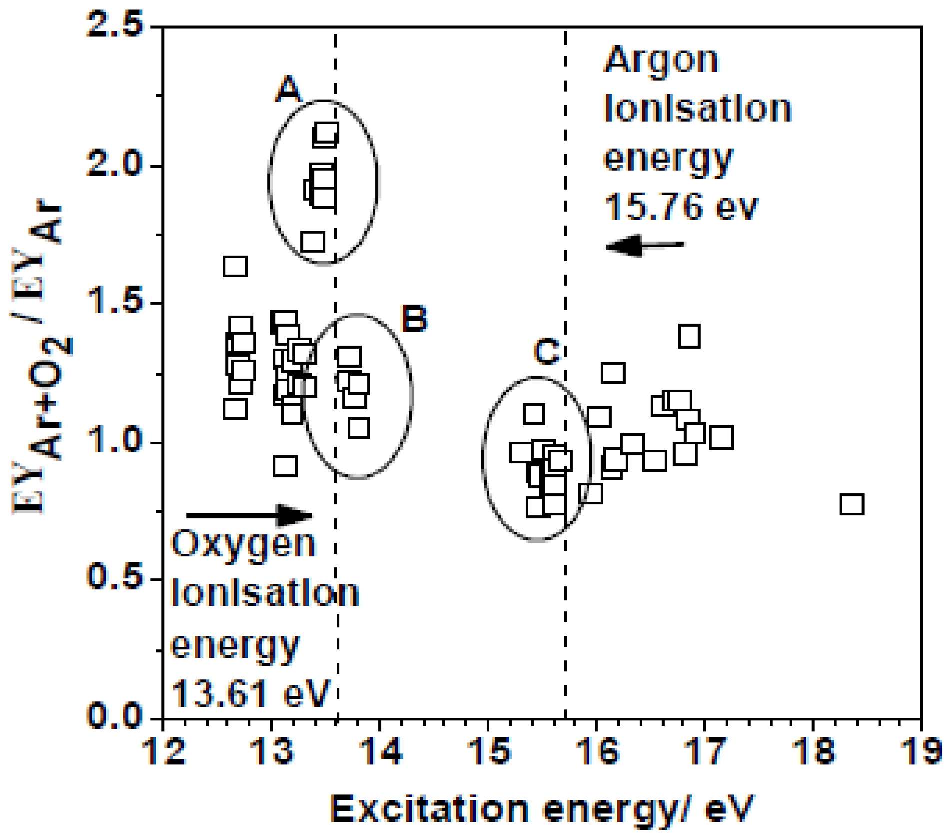
{CT + cascade
{PI
{EI

ADDED OXYGEN (Sohail Mushtaq)

Two approaches – plot against upper energy level for fixed oxygen content, OR plot intensity of individual lines against oxygen concentration.

ACT by the added gas –
5 years ago, paper by Steers, Smid & Weiss on H-ACT. -selective excitation at 13.6 eV.
Sohail Mushtaq has observed O-ACT also at 13.61 eV., most obvious in neon. Also with neon. ACT is produced by the metastable ^2D O^+ state at 16.93 eV

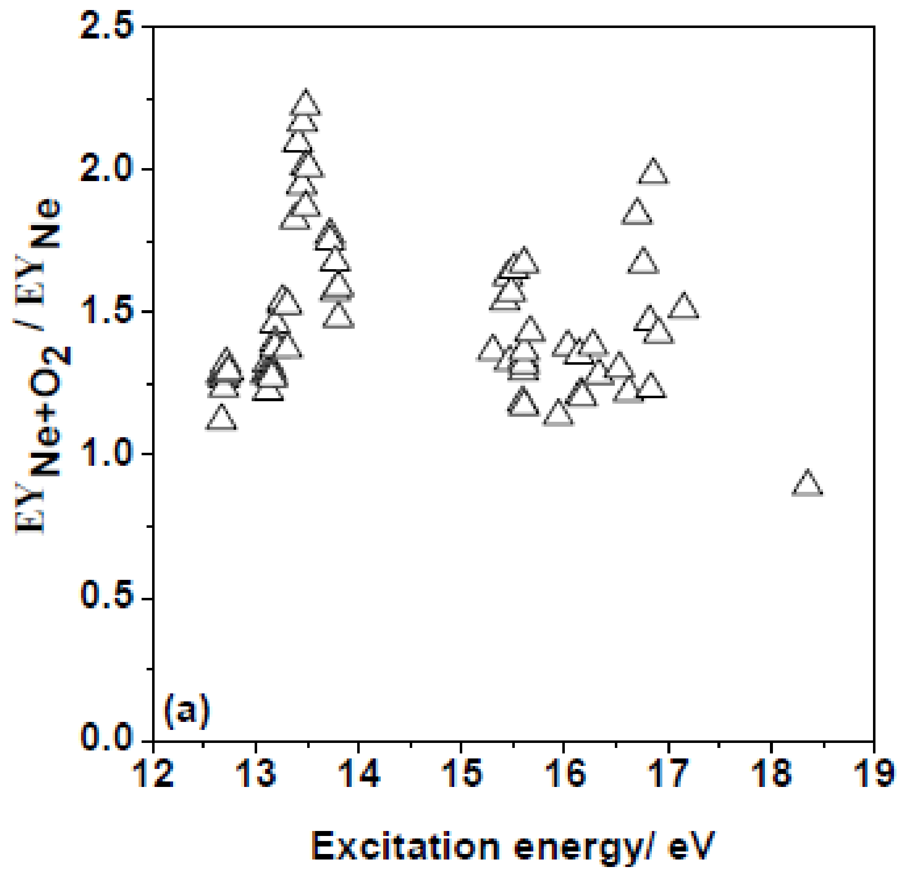
Oxygen ACT (O-ACT)



4 mm anode tube.
700V, 40 mA

0.20 % v/v oxygen added to argon; iron sample

0.04 % v/v oxygen added to neon .(iron sample)
Note the ACT by oxygen ionic metastable state at 16.93 eV.



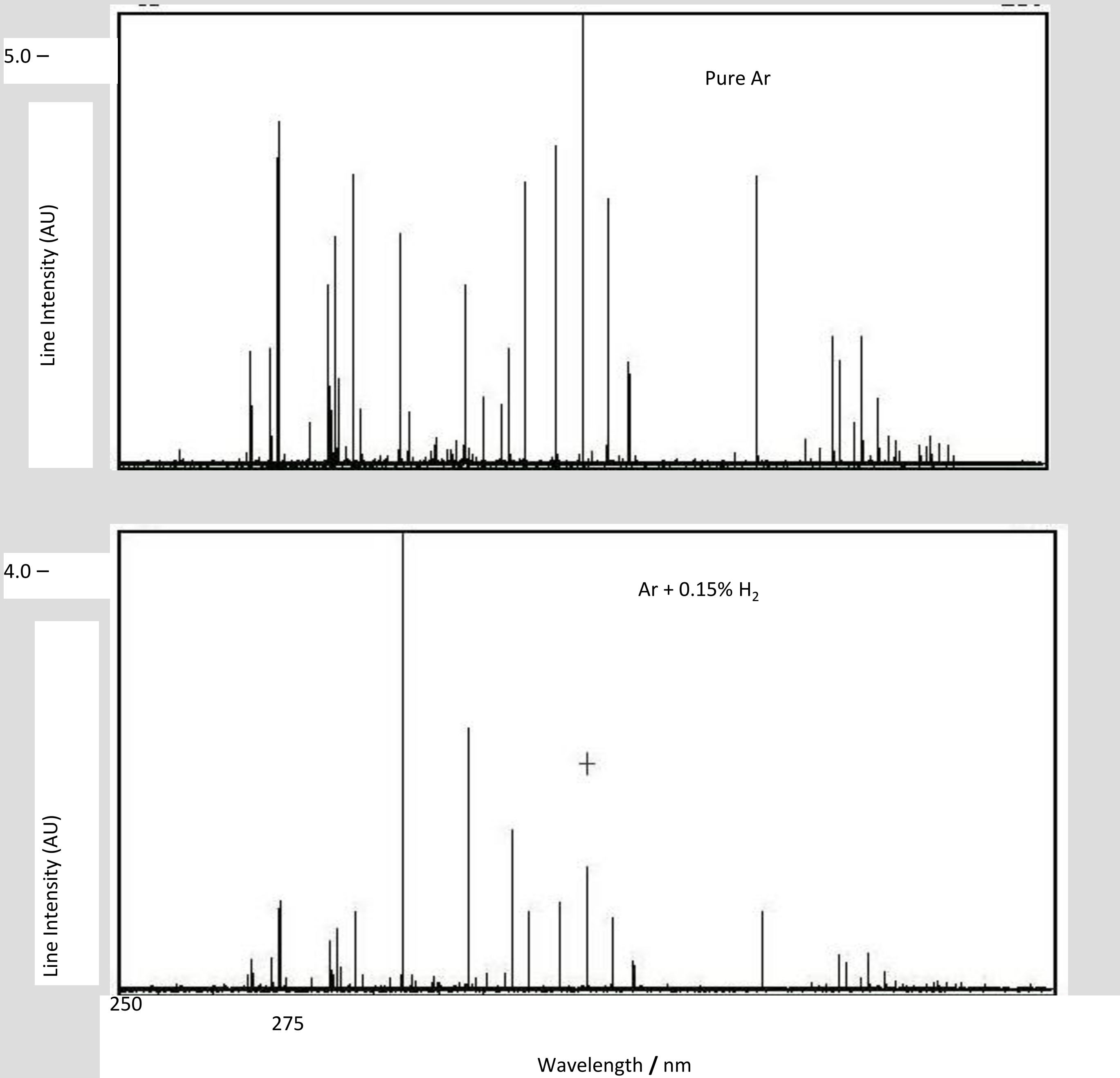


Fig. 1. A section of the manganese spectrum excited in argon and in an argon/hydrogen plasma

LONDON metropolitan university

And in practical analysis??

Binary alloys - competition for argon ions

Aluminium/zinc. Copper/zinc (Weiss)

Be very cautious of ionic lines, total excitation energy ~13.0-13.6 eV and ~15.4-16.0 eV

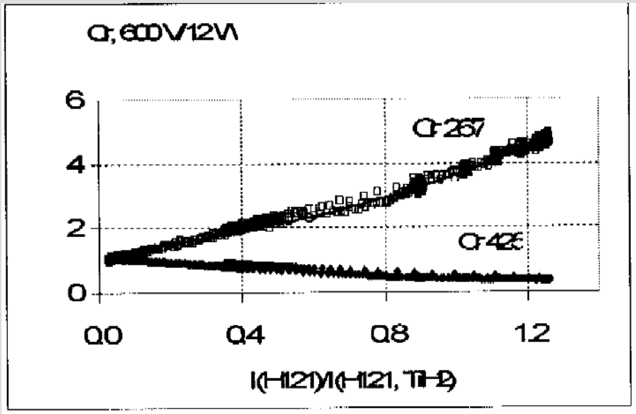
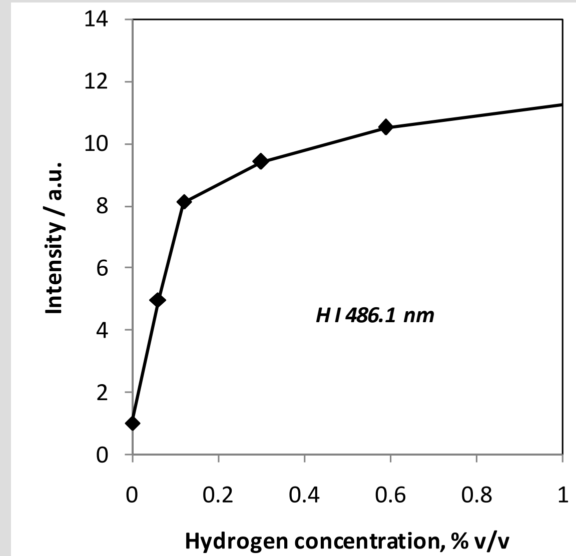
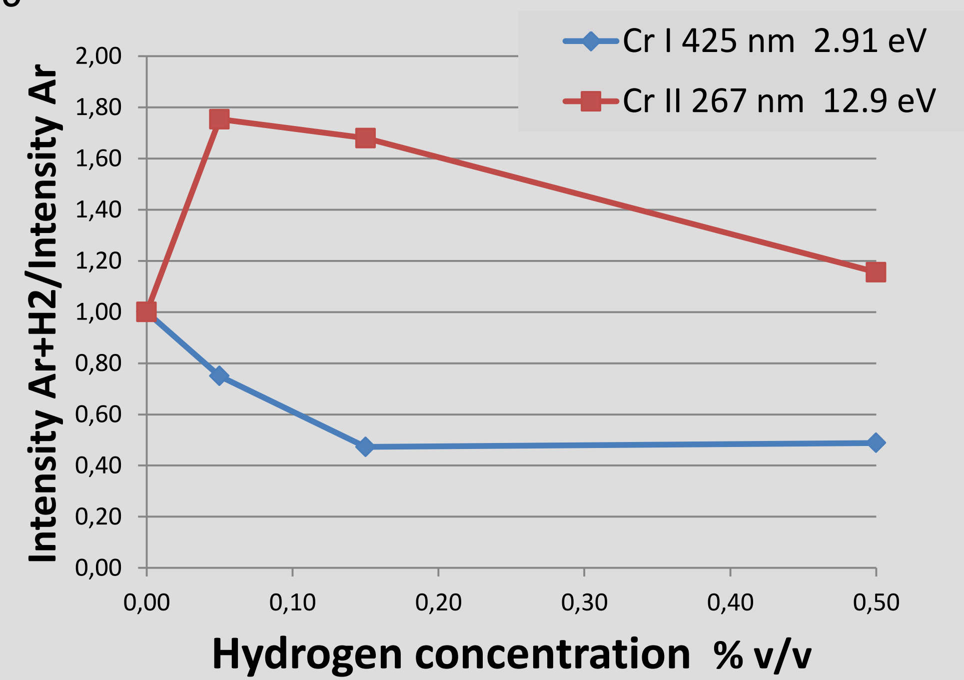


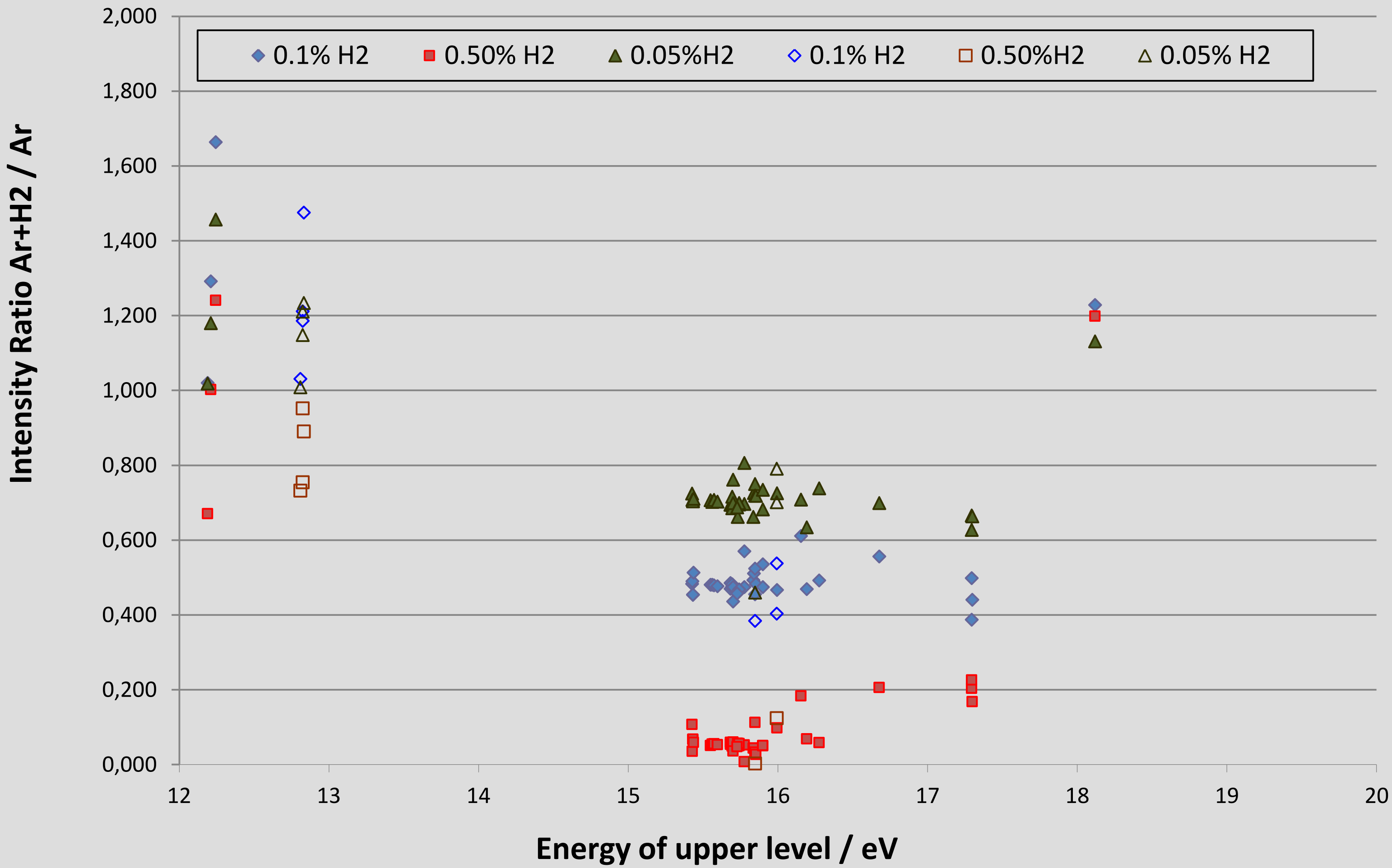
Fig. 3 Emission yields variation with hydrogen for two Cr lines.

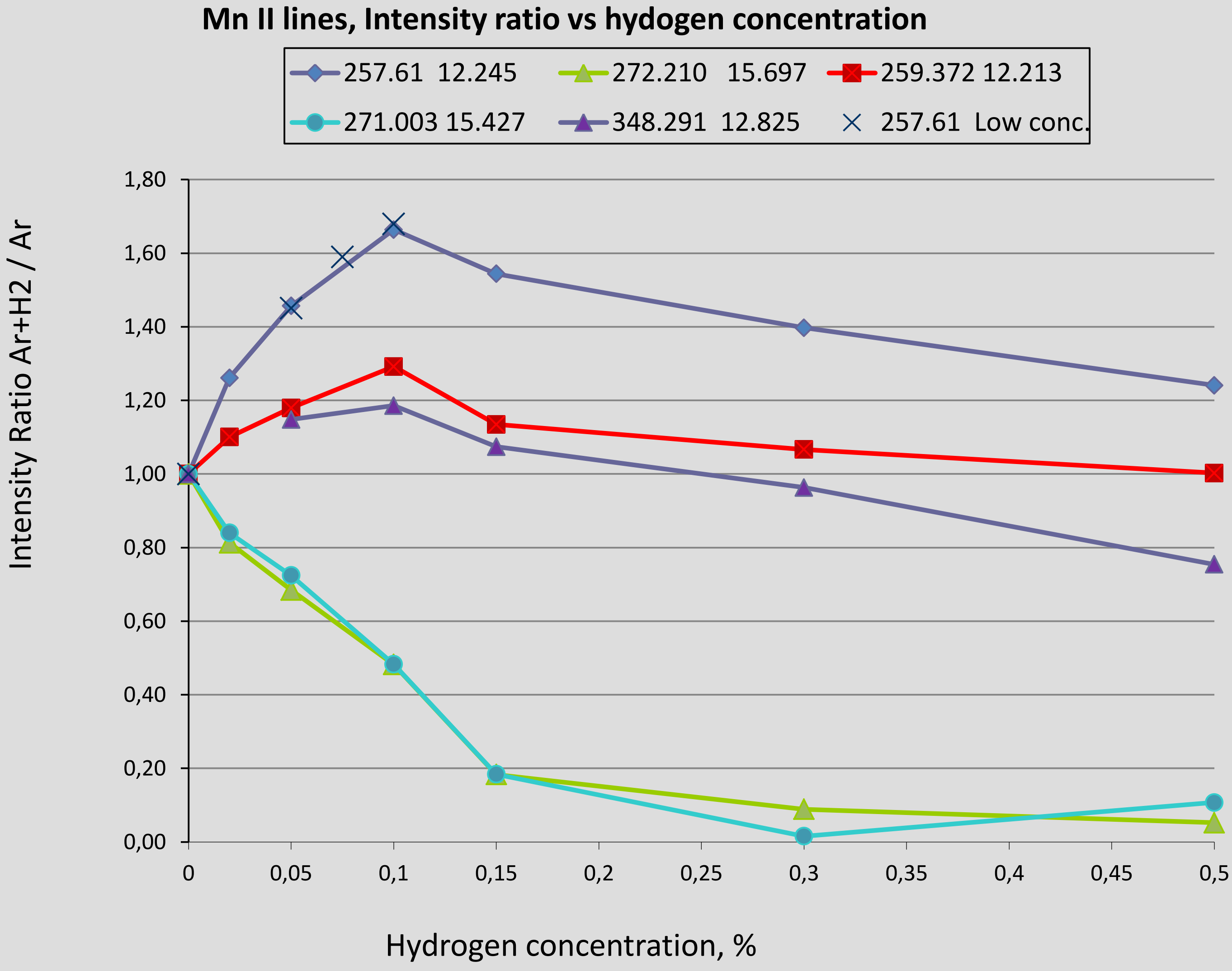


A. Bengtson & S. Hanstrom , *ISIJ International*, 2002, **42,** 82-86.

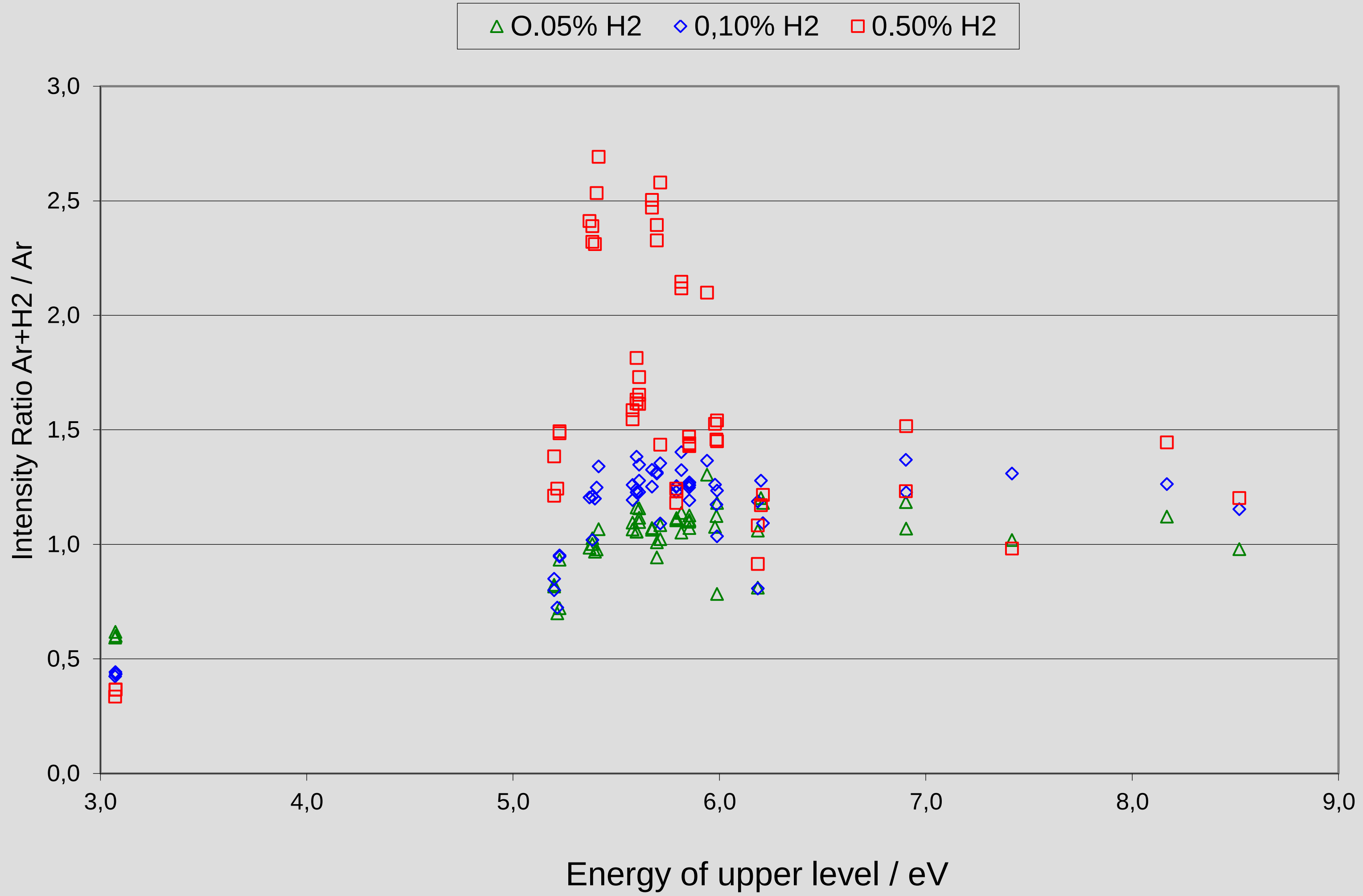


Mn II lines, Intensity ratio vs energy of upper level

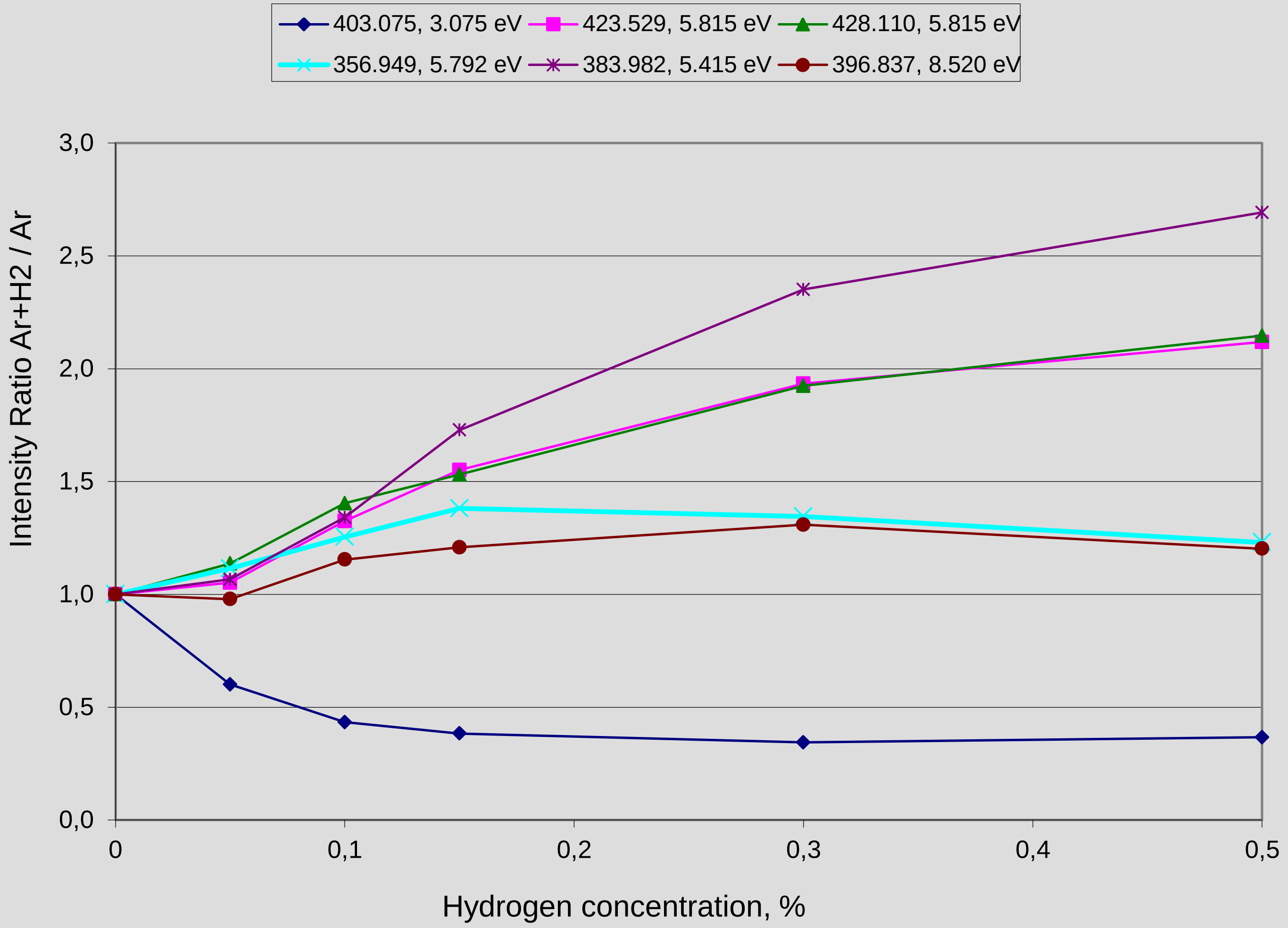



Mn II lines, Intensity ratio vs hydogen concentration
257.61 12.245
272.210 15.697
259.372 12.213
271.003 15.427
348.291 12.825
257.61 Low conc.
Intensity Ratio Ar+H2 / Ar
1,80
1,60
1,40
1,20
1,00
0,80
0,60
0,40
0,20
0,00
0
0,05
0,1
0,15
0,2
0,25
0,3
0,35
0,4
0,45
0,5
Hydrogen concentration, %

Mn I lines, Intensity ratio vs energy of upper level



Mn I lines, Intensity ratio vs hydrogen concentration



CONCLUSIONS

The more you look, the more you find!!

In OES, the existence of selective excitation mechanisms in Glow Discharges (NOT IN THERMAL EQUILIBRIUM!) means that individual spectral lines are affected in differing ways by changes in the plasma gas or the presence of molecular gases (H_2 and O_2).

Magnitude of the effects differ with discharge conditions.

Many, but not all, of the effects become significant at molecular gas concentration higher than those occurring in analytical practice.

Vielen Dank für Ihre Aufmerksamkeit!