Spuren molekularer Gase in GD Plasmen - neue Entwicklungen

E.B.M. Steers,

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, LondonMet.)

Many thanks to these coworkers, and to the EC for funding the Gladnet Research Training Network, 2007-2011, (Contract No. MRTN-CT-2006-035459)

LONDON metropolitan university

Main topics

- Effect of added hydrogen with argon
- Effect of added hydrogen with neon
- Effect of added oxygen with argon
- Effect of added oxygen with neon
- GD-MS with high resolution Thermo Element GD
- GD-MS with GD-ToF MS instrumentation (EMPA)

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

Considering the experiment B in more detail**:**.

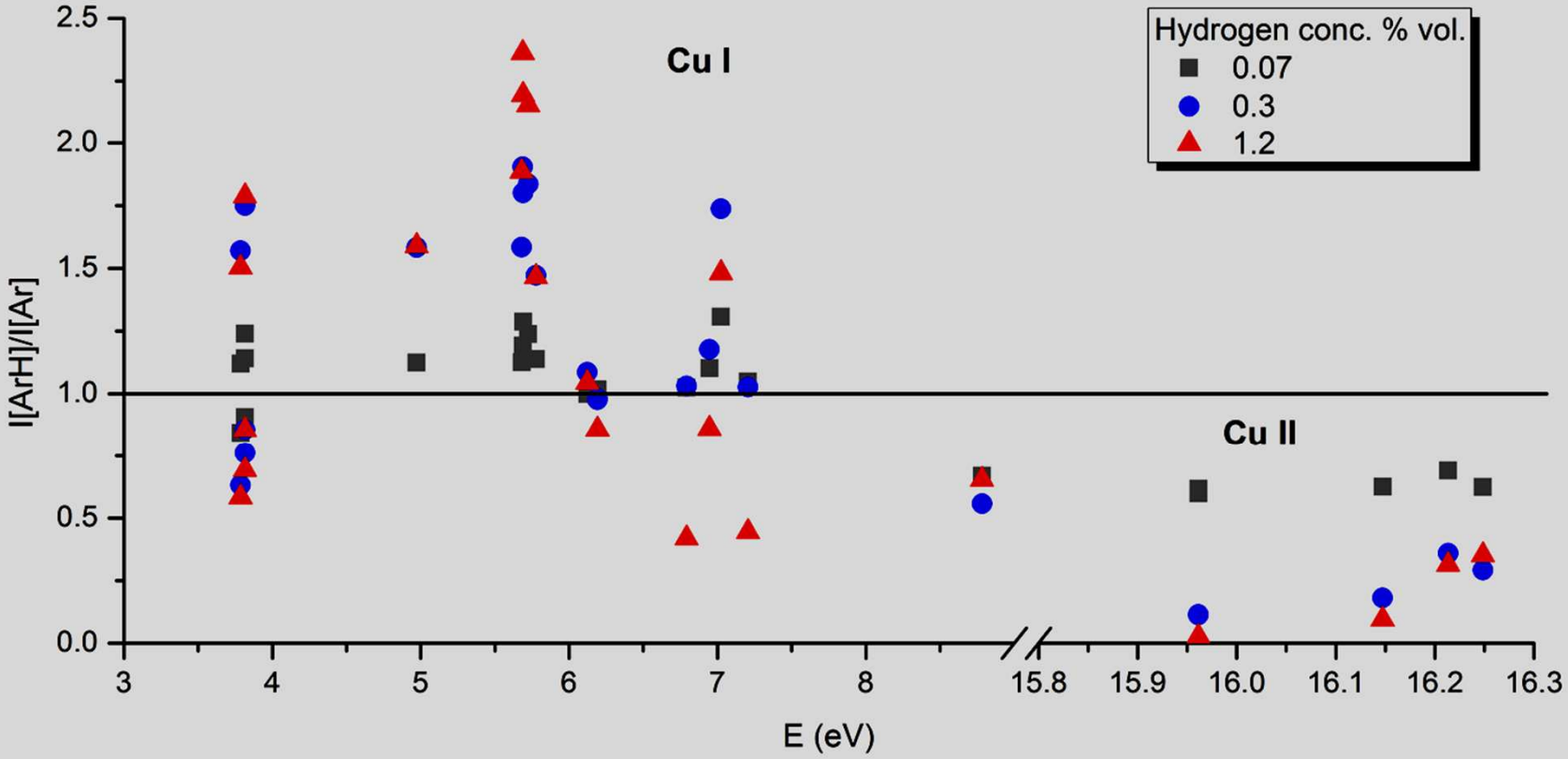
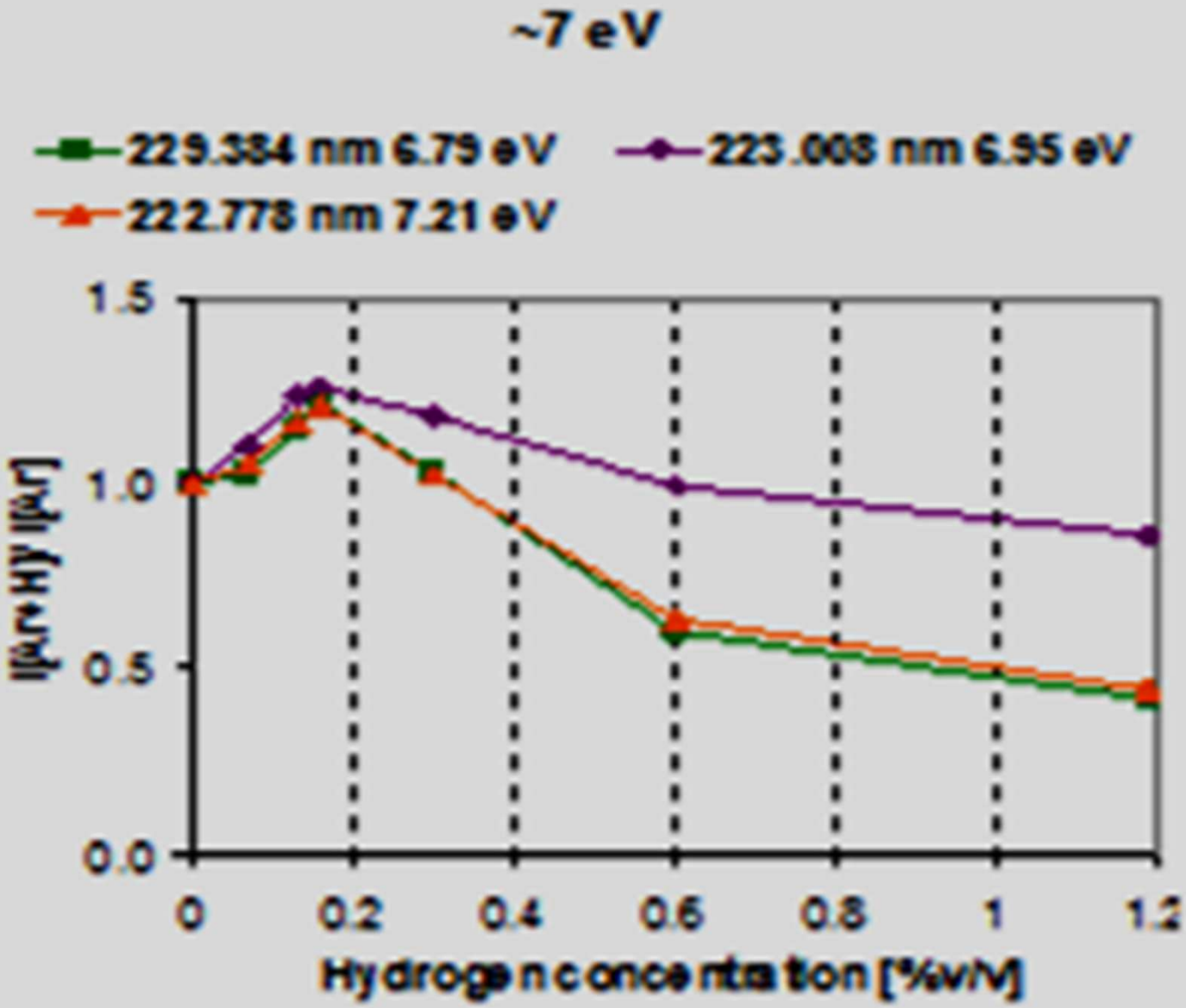


Figure: 4.4 Intensity ratios I(ArH)/ I(Ar) for copper atomic and ionic lines with three different Ar/H_2 mixtures (0.07, 0.3 and 1.2 % H_2) plotted against upper energy levels of those copper lines

Looking first at lines with upper energy 7 eV

LONDON metropolitan university



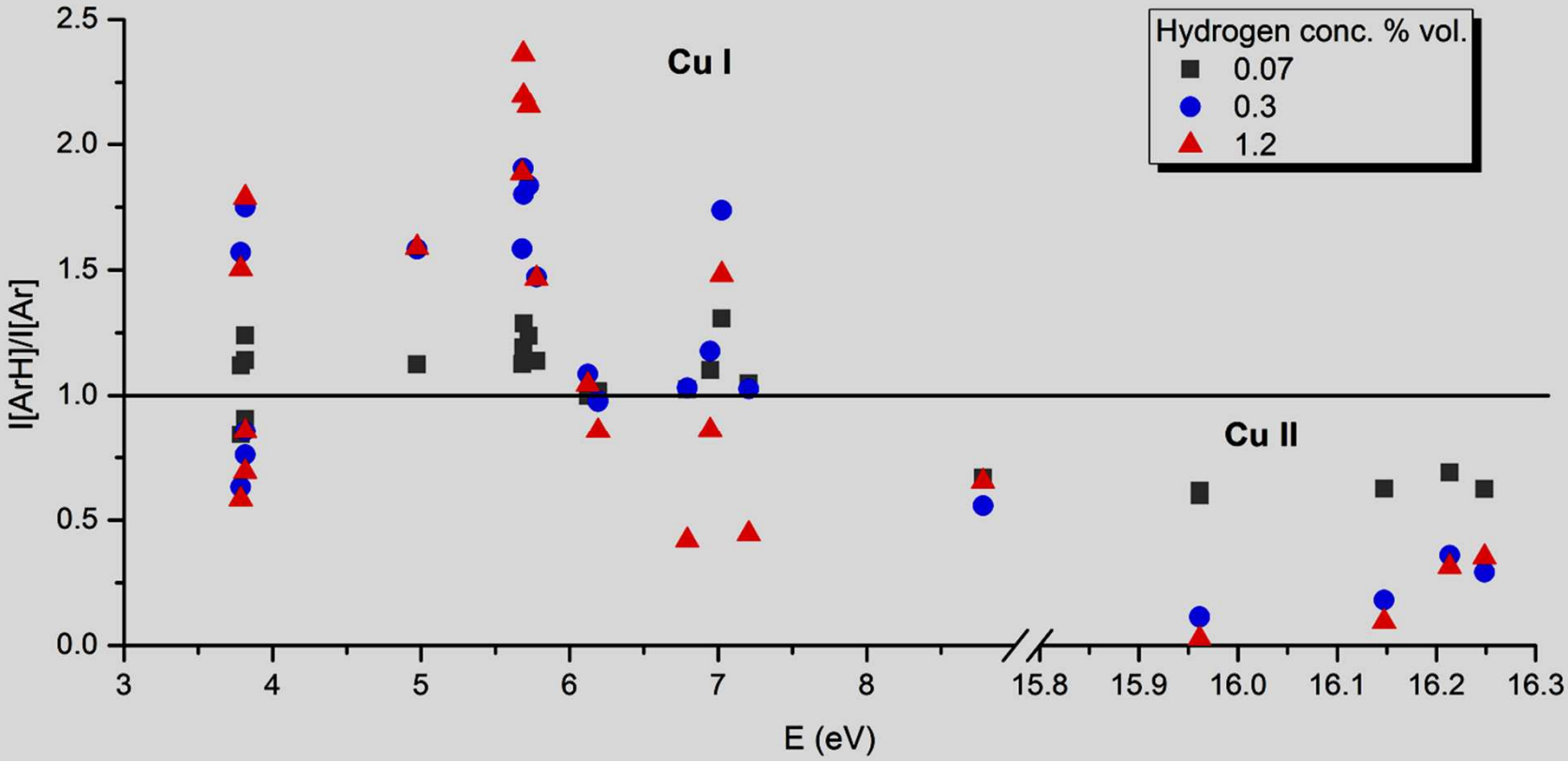


Figure: 4.4 Intensity ratios I(ArH)/ I(Ar) for copper atomic and ionic lines with three different Ar/H_2 mixtures (0.07, 0.3 and 1.2 % H_2) plotted against upper energy levels of those copper lines

Now at Cu II lines

Asymmetric Charge Transfer (ACT) Ionisation:

$$G^{+} + M \Rightarrow G_{o} + M^{+*} + \Delta E$$

PROCESS ONLY POSSIBLE IF ΔE IS SMALL
i.e. RESONANT PROCESS

where G represents gas. Ar, Ne.....; M sample species Cu. Fe .....
* an excited state, and $_{o}$ the ground state.

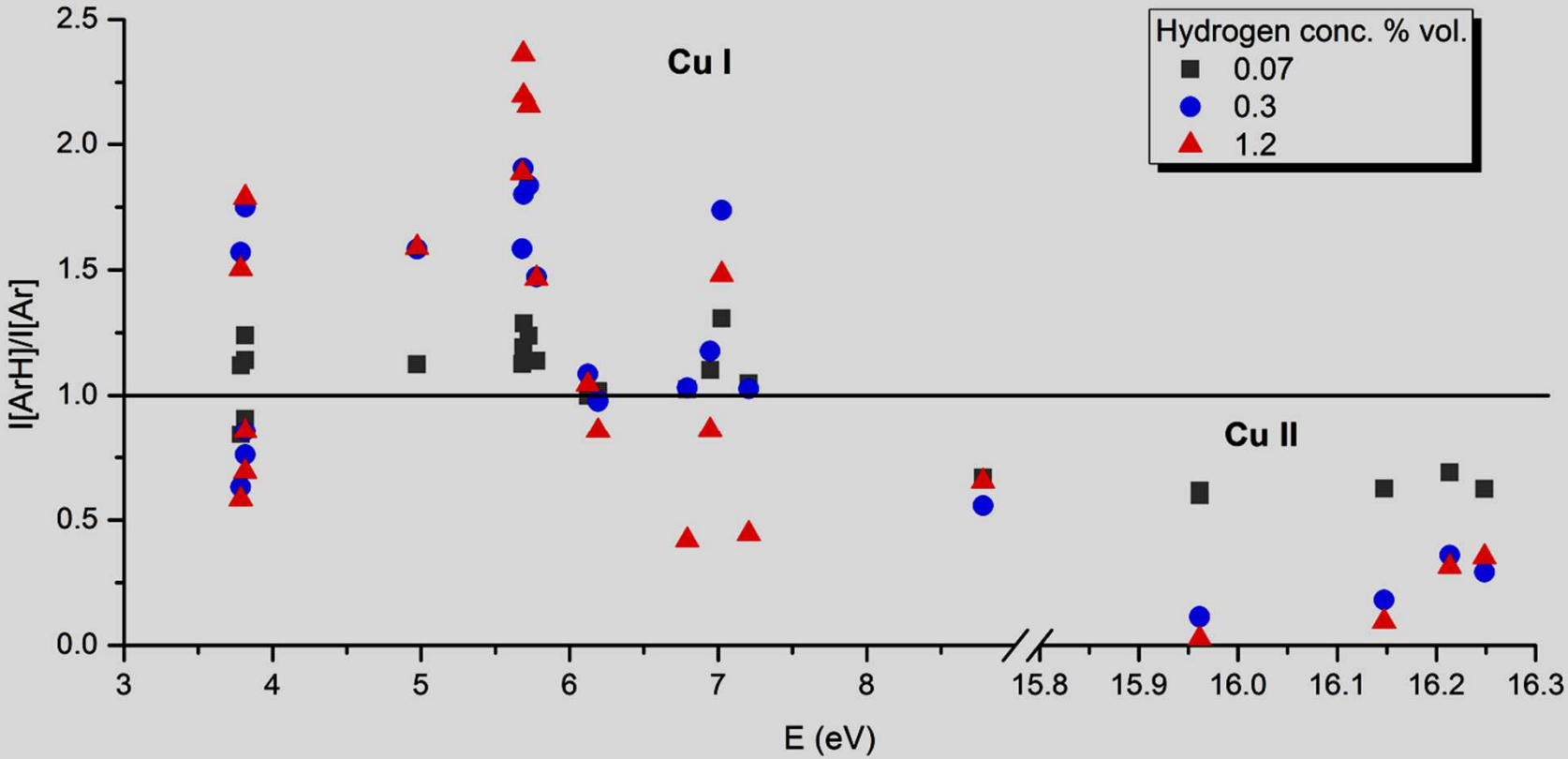
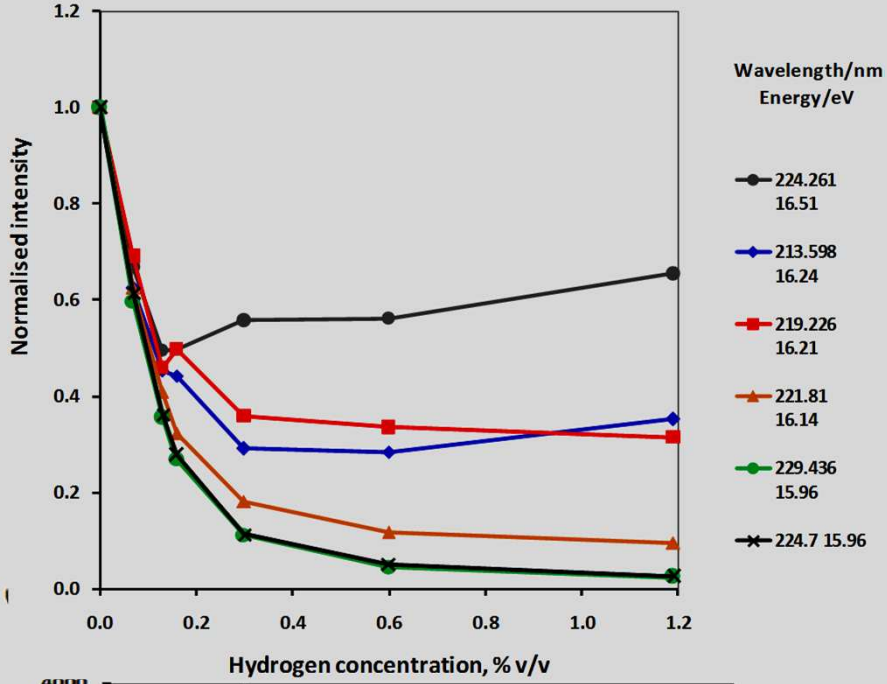
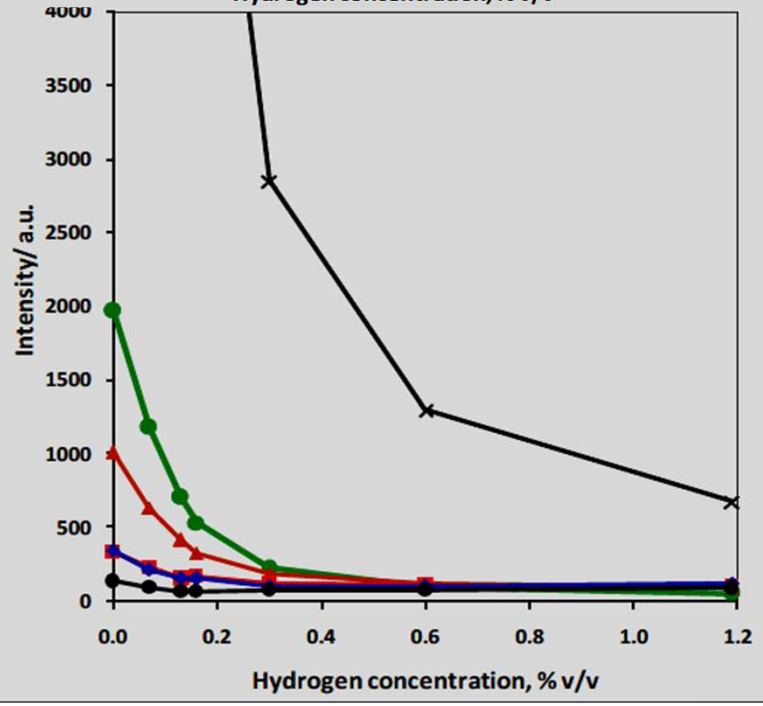
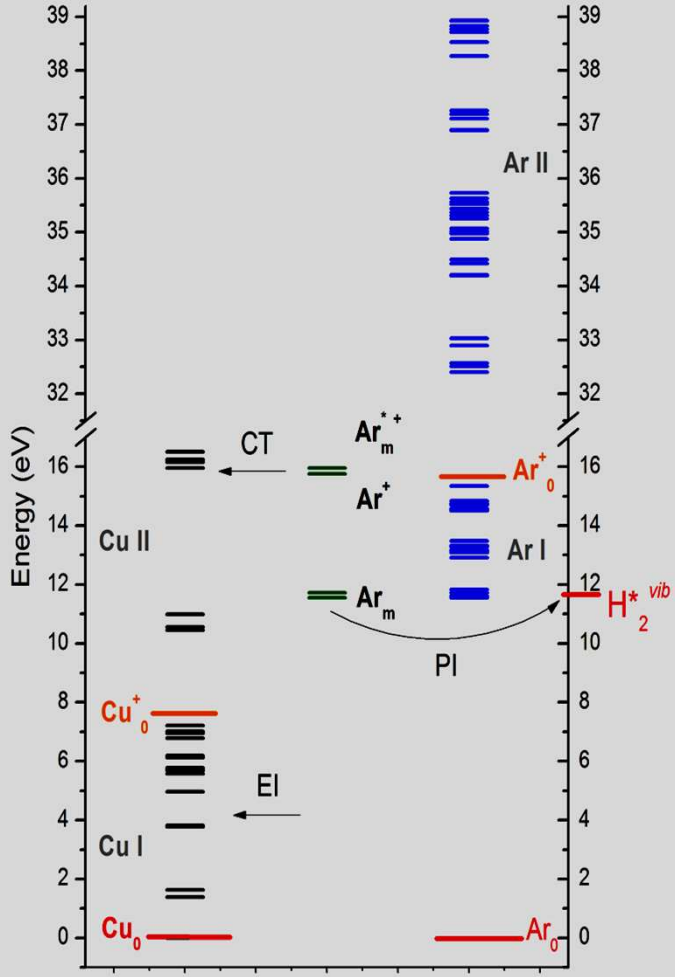


Figure: 4.4 Intensity ratios I(ArH)/ I(Ar) for copper atomic and ionic lines with three different Ar/H_2 mixtures (0.07, 0.3 and 1.2 % H_2) plotted against upper energy levels of those copper lines





Energy change/eV	Wavelength /nm
2	625
3	417
4	312
5	250
6	208



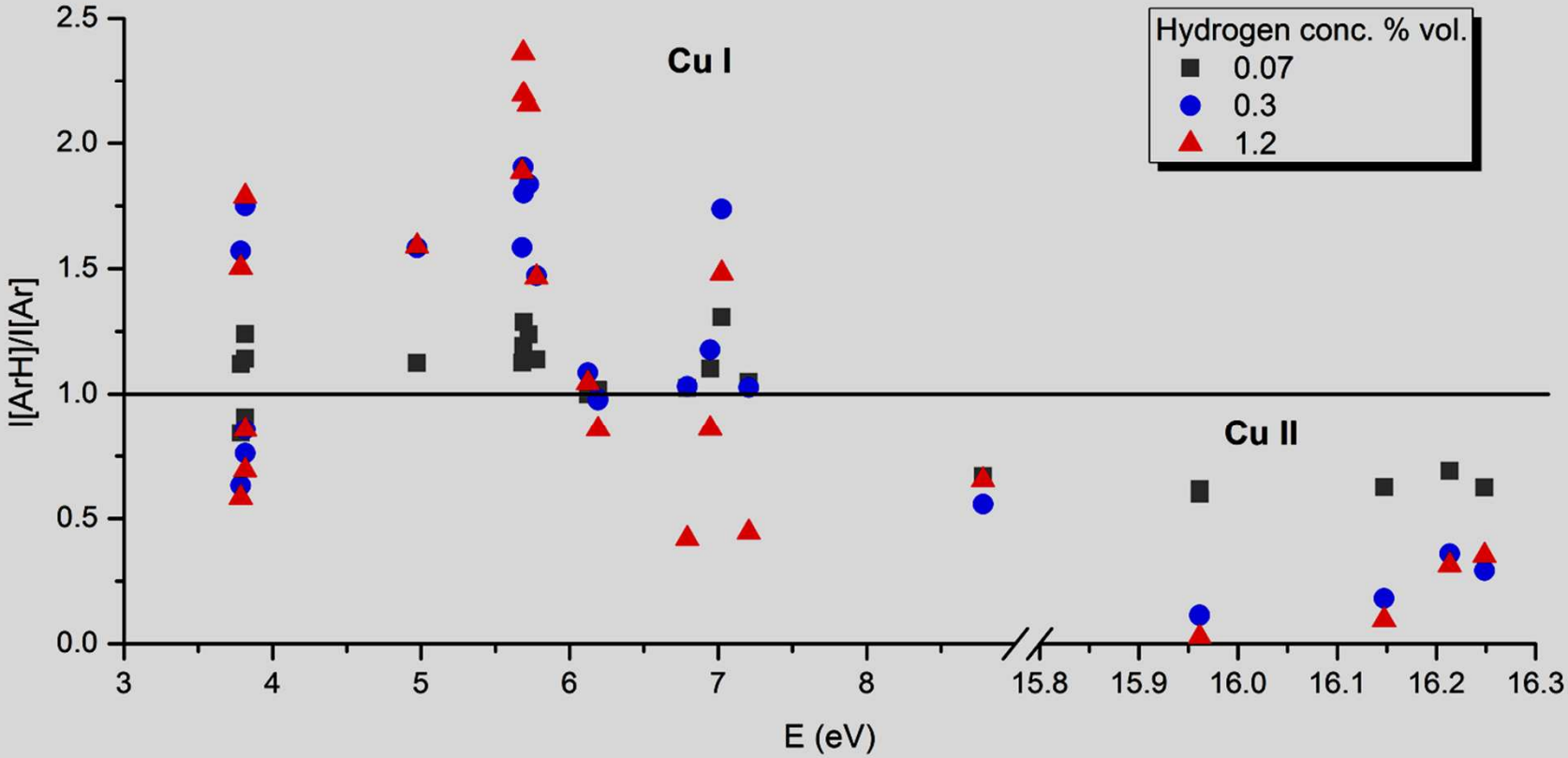
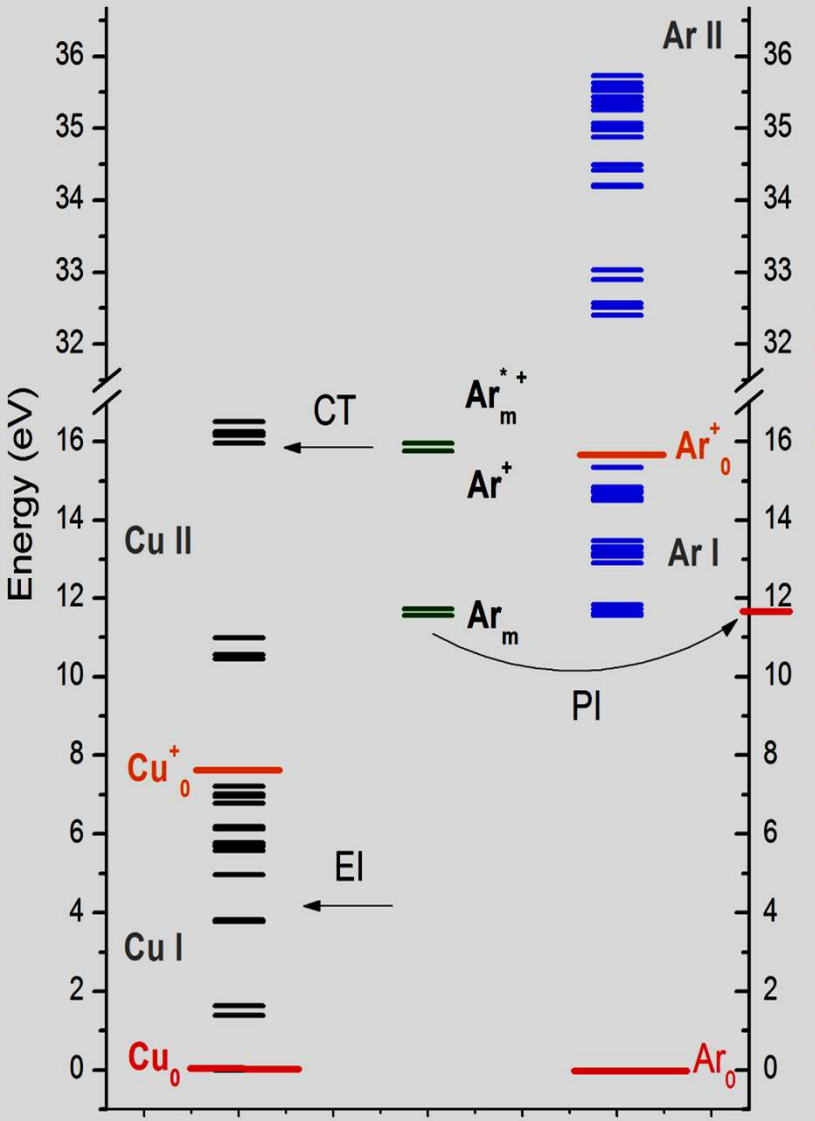
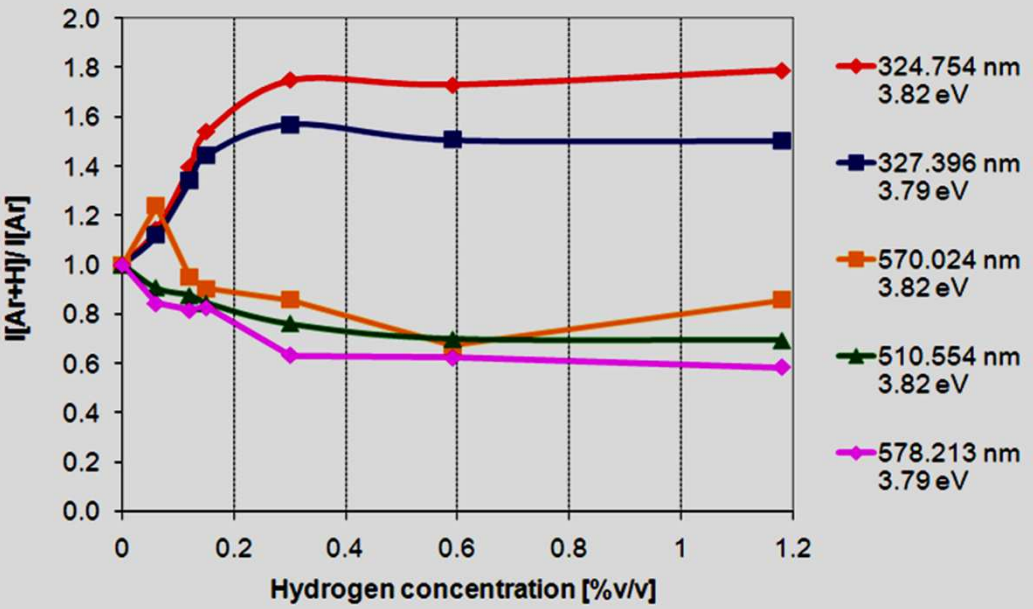


Figure: 4.4 Intensity ratios I(ArH)/ I(Ar) for copper atomic and ionic lines with three different Ar/H_2 mixtures (0.07, 0.3 and 1.2 % H_2) plotted against upper energy levels of those copper lines

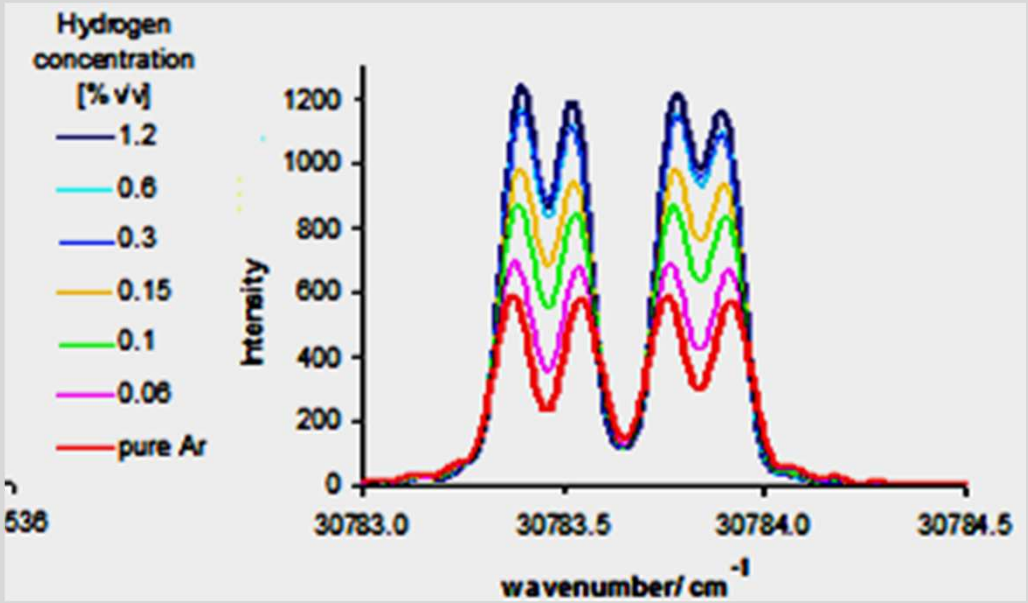
Looking now at the resonance lines

LONDON metropolitan university



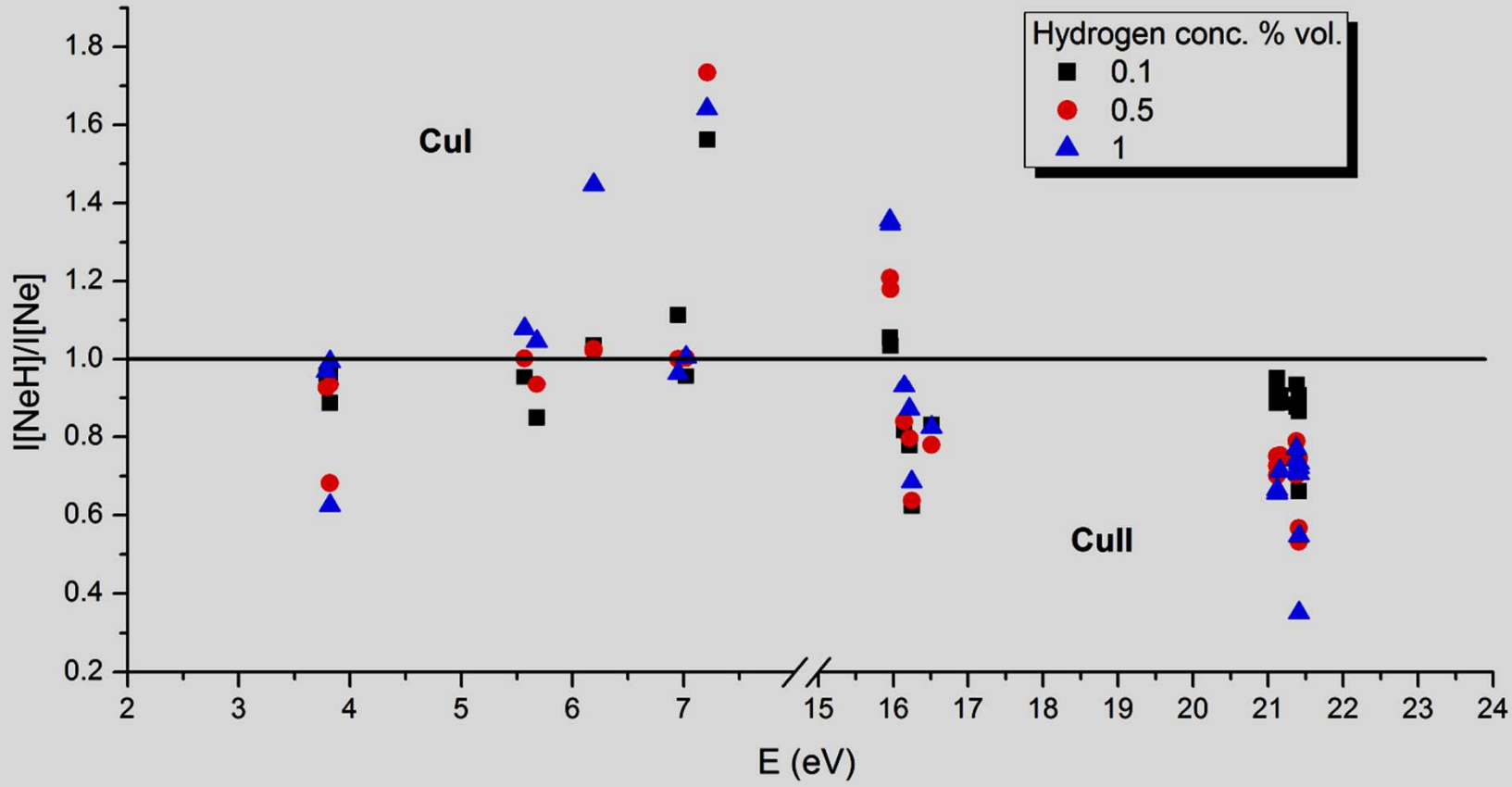


Energy change/eV	Wavelength /nm
2	625
3	417
4	312
5	250
6	208

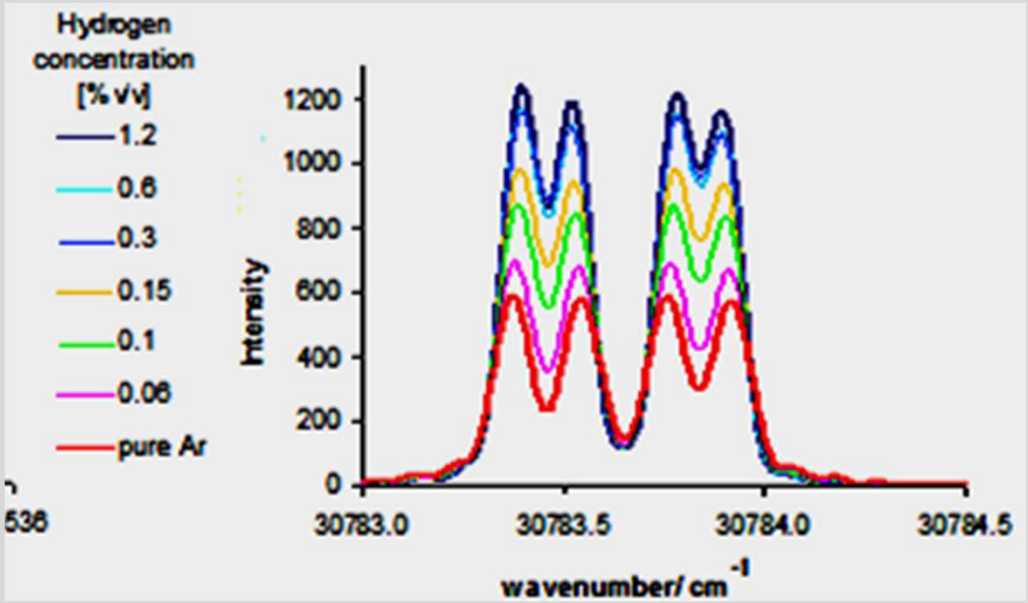


Cu I, 324.8 nm
Argon + hydrogen
700 V, 20 mA,
pressure about 8 hPa

Under these conditions, significant drop in sputter rate

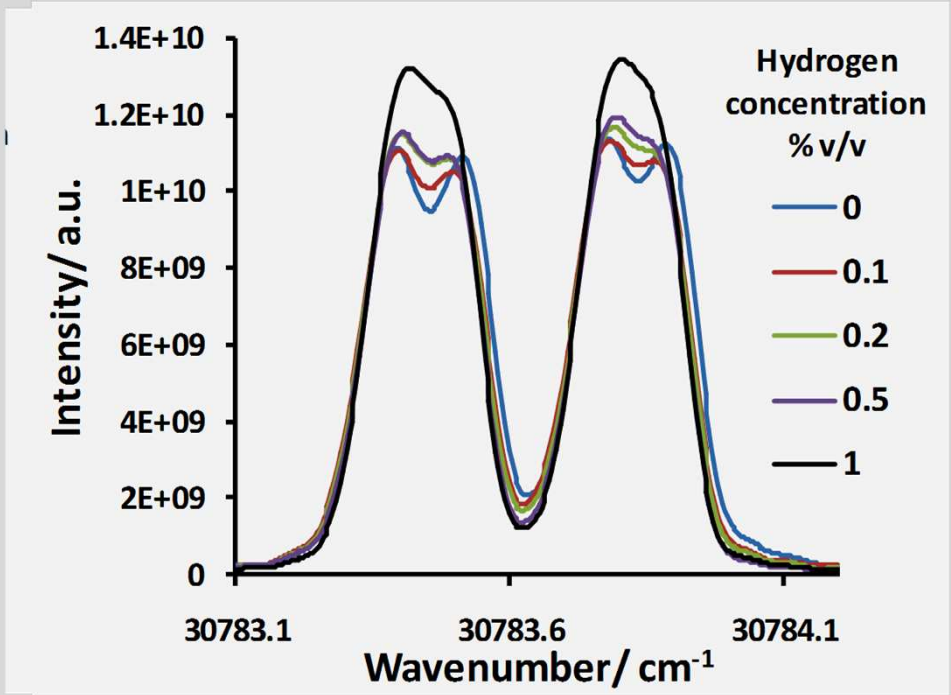


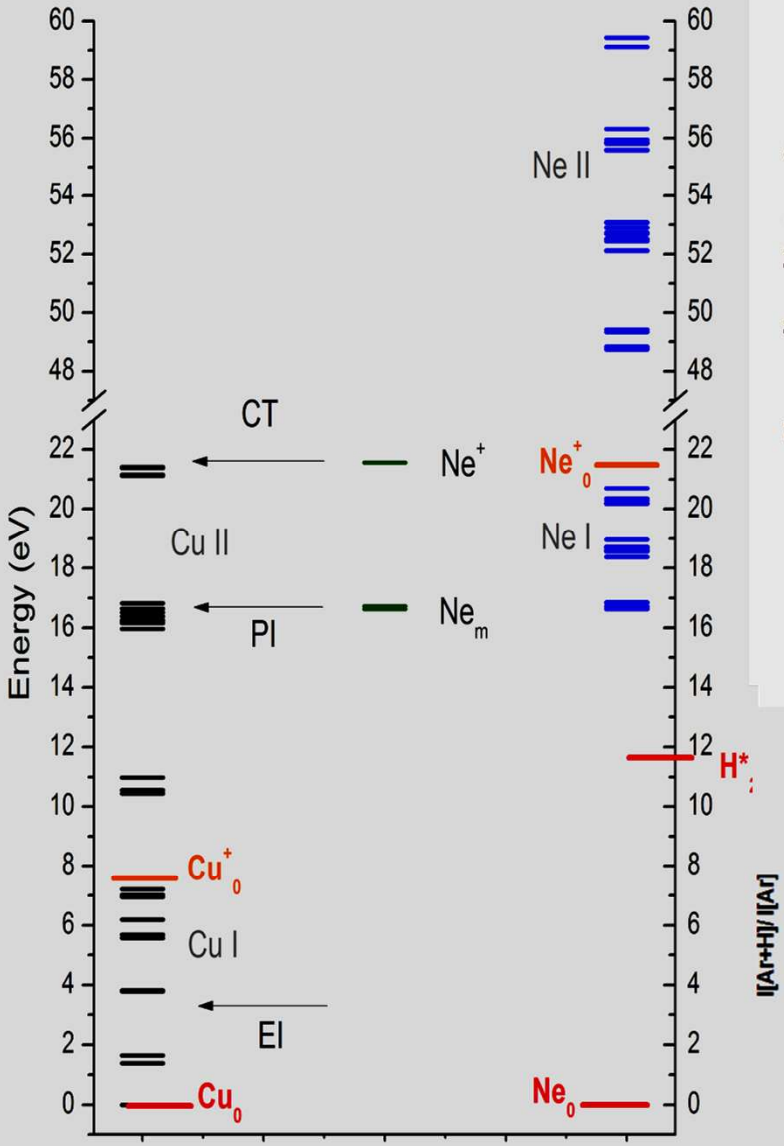
Observed intensity ratios when hydrogen is added to a **NEON** plasma. Firstly resonance lines.

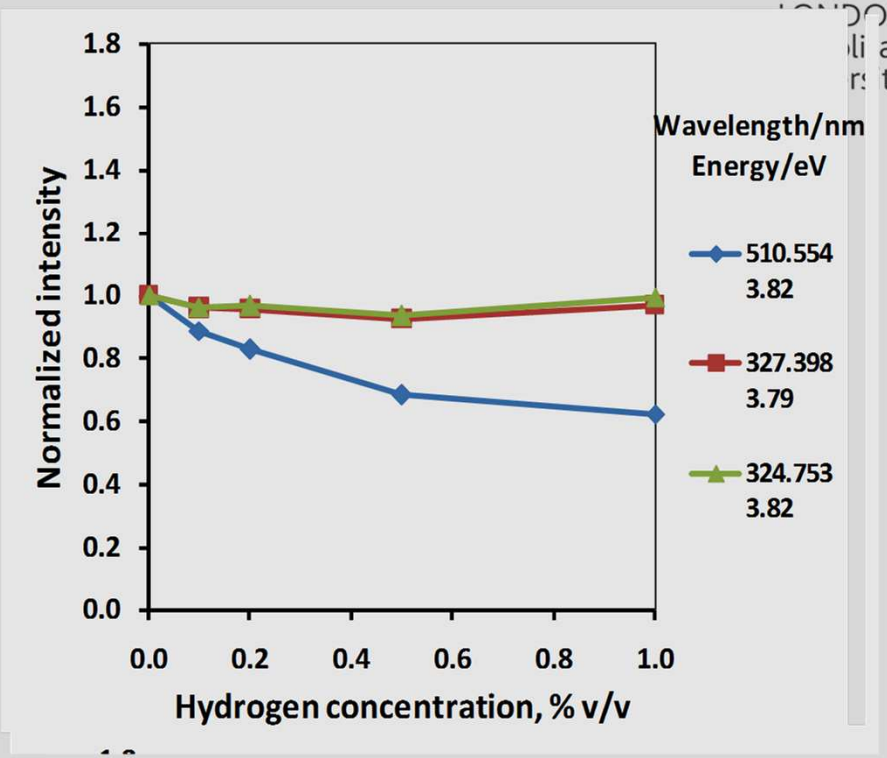


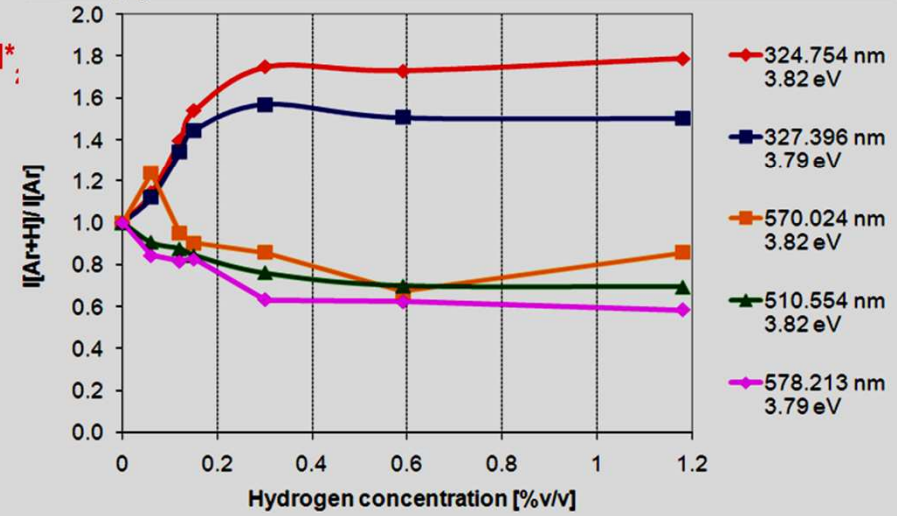
Cu I, 324.8 nm
Argon + hydrogen
700 V, 20 mA,
pressure about 8 hPa

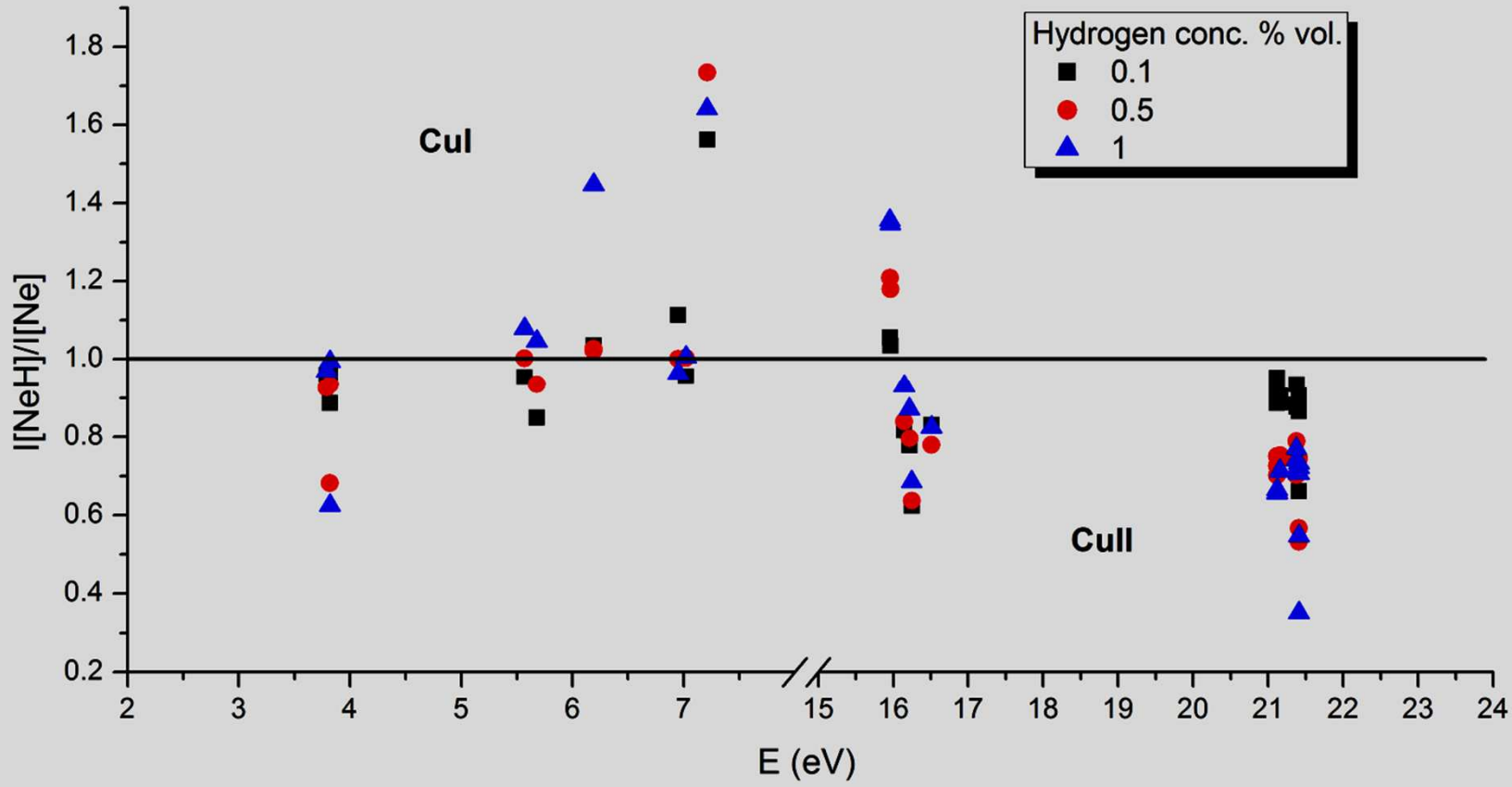
Cu I, 324.8 nm
Neon + hydrogen
700 V, 20 mA,
pressure about 14 hPa



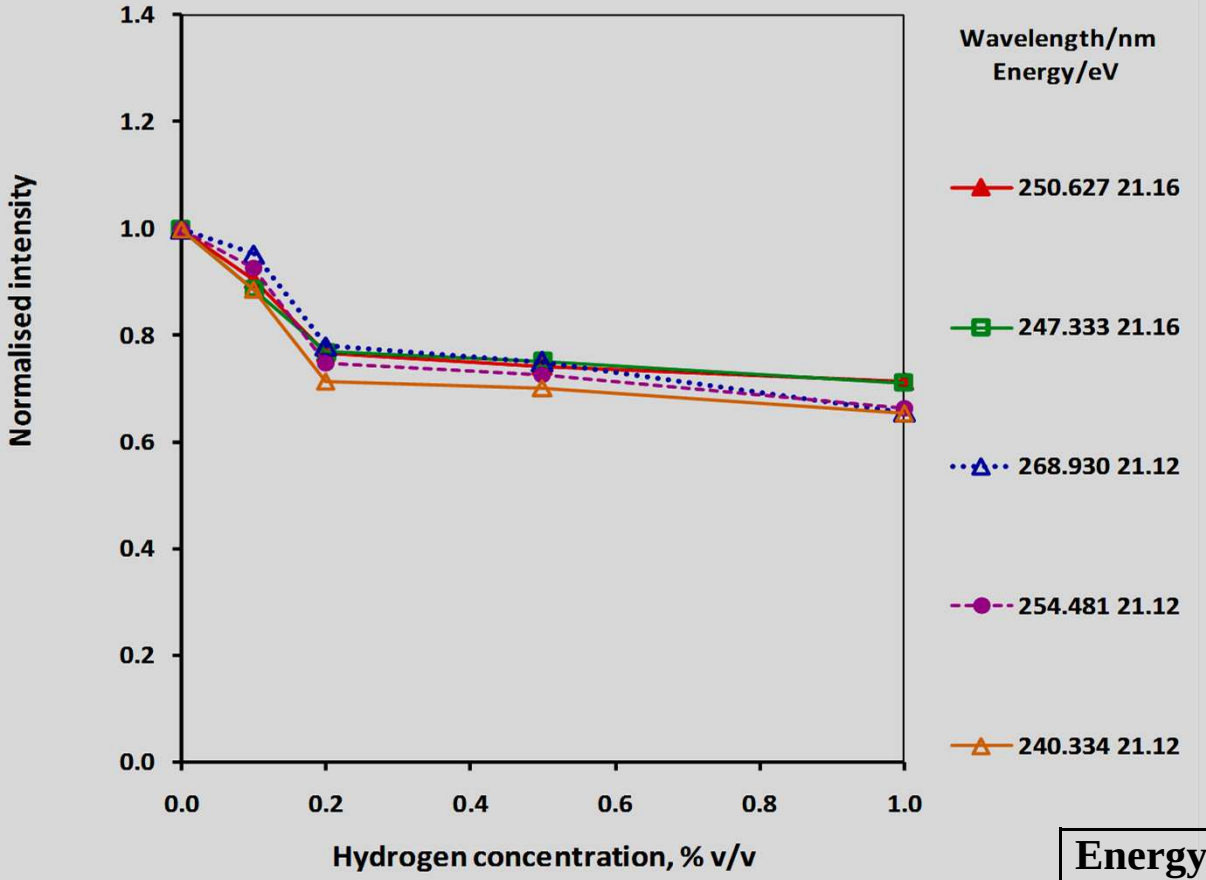

Energy (eV)
CT
Cu II
PI
EI
Cu I
Ne II
Ne I
Ne+
Nem
Cu+0
Cu0
Ne+0
Ne0
H*


Normalized intensity
Hydrogen concentration, % v/v
Wavelength/nm
Energy/eV
510.554
3.82
327.398
3.79
324.753
3.82

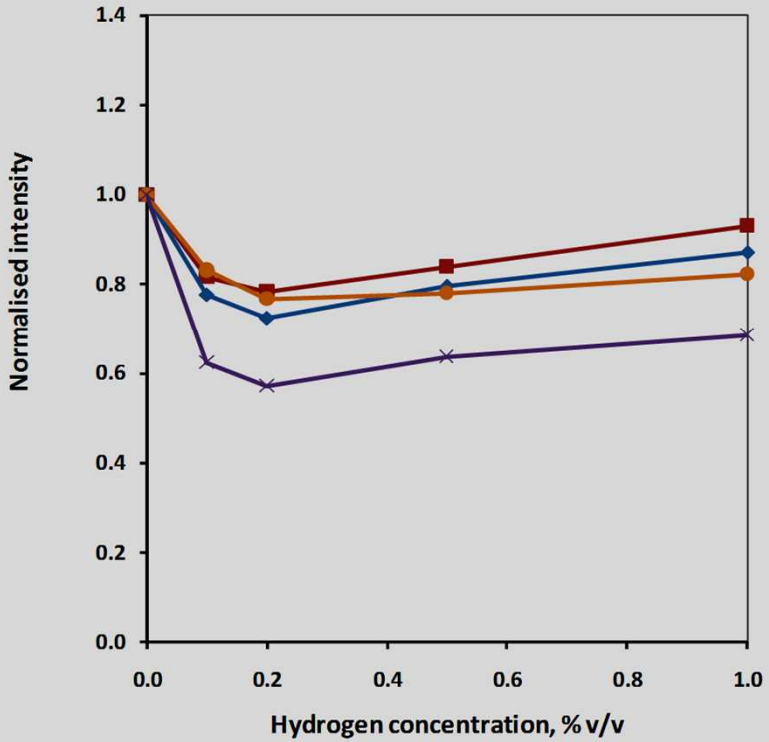

I[Ar+H]/ I[Ar]
Hydrogen concentration [%v/v]
324.754 nm
3.82 eV
327.396 nm
3.79 eV
570.024 nm
3.82 eV
510.554 nm
3.82 eV
578.213 nm
3.79 eV

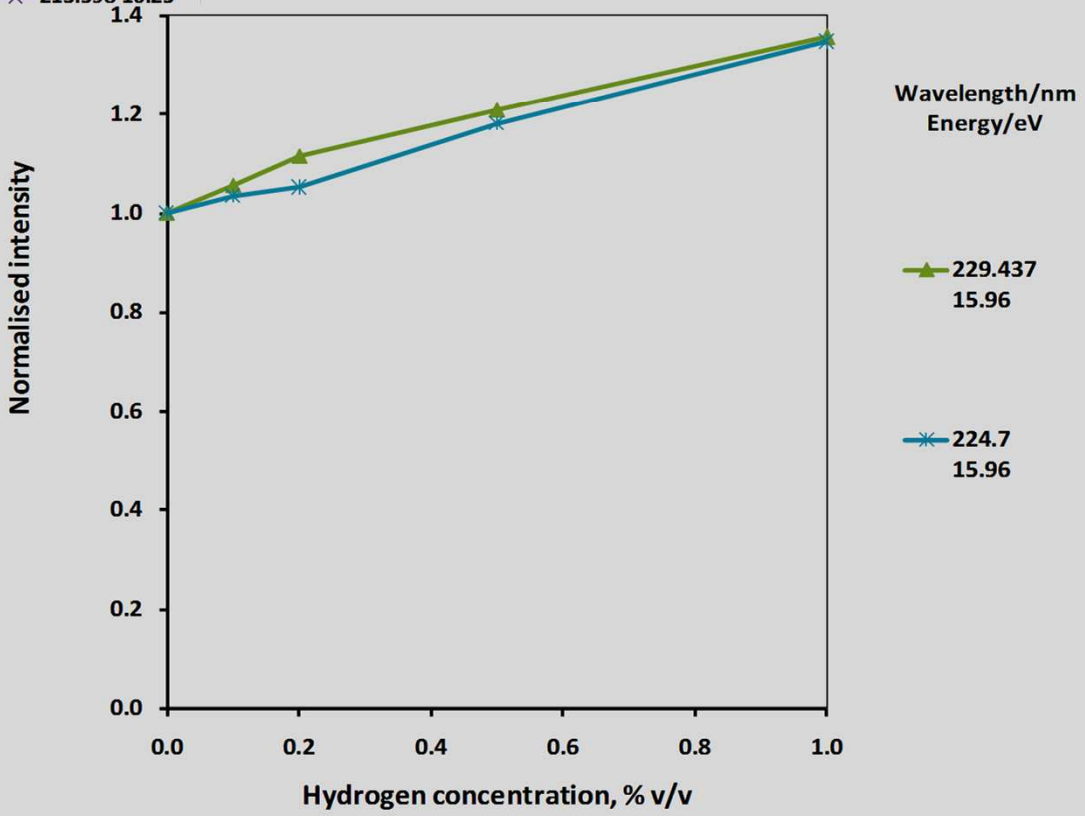


Observed intensity ratios when hydrogen is added to a **NEON** plasma. Now lines excited by ACT.



Energy change/eV	Wavelength /nm
2	625
3	417
4	312
5	250
6	208


Normalised intensity
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
Hydrogen concentration, % v/v
Wavelength/nm
Energy/eV
221.811 16.15
219.227 16.22
224.261 16.51
213.598 16.25


Normalised intensity
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
Hydrogen concentration, % v/v
Wavelength/nm
Energy/eV
229.437
15.96
224.7
15.96

Asymmetric Charge Transfer (ACT) Ionisation:

$$G^{+} + M \Rightarrow G_o + M^{+*} + \Delta E$$

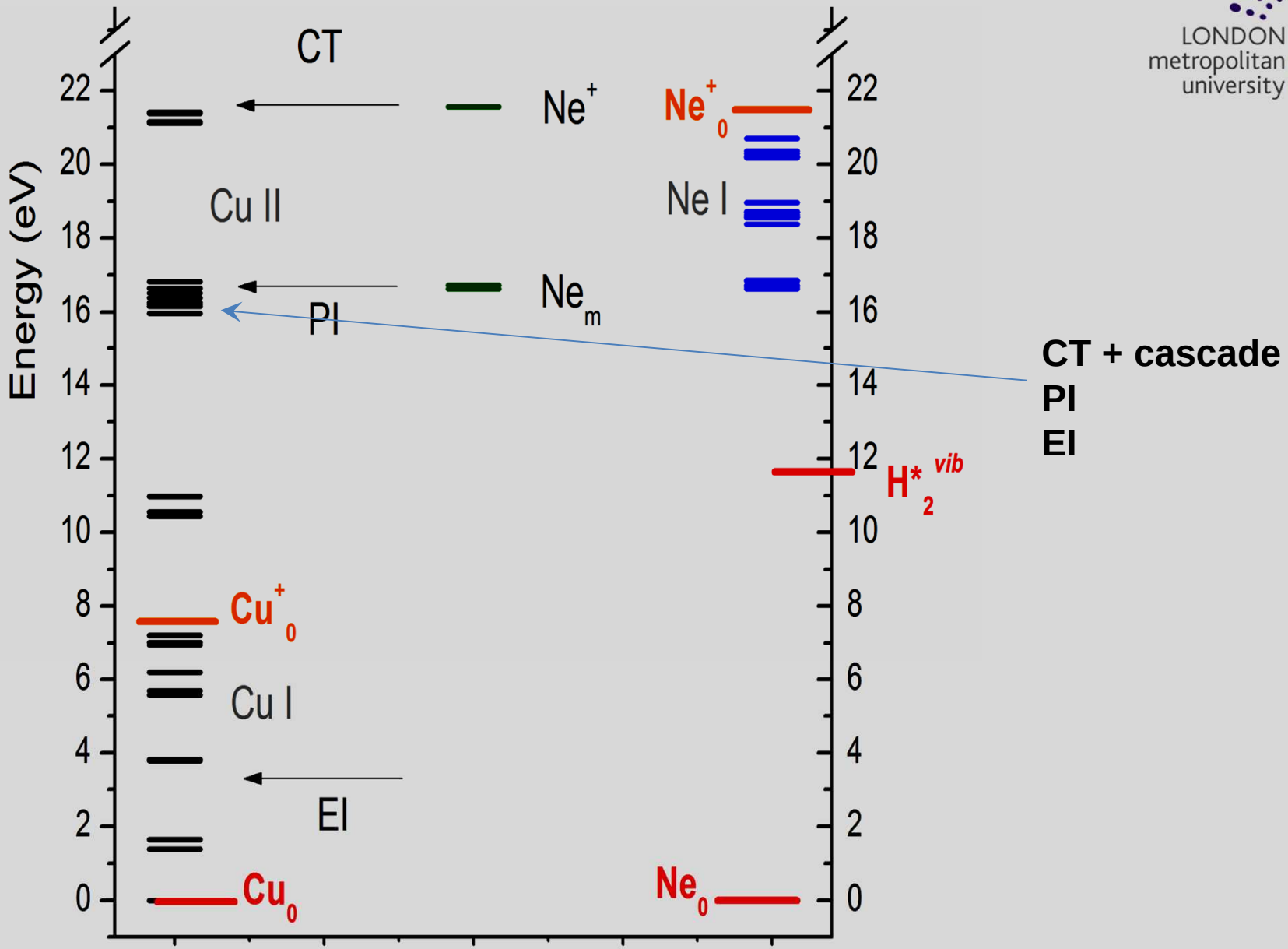
PROCESS ONLY POSSIBLE IF ΔE IS SMALL
i.e. RESONANT PROCESS

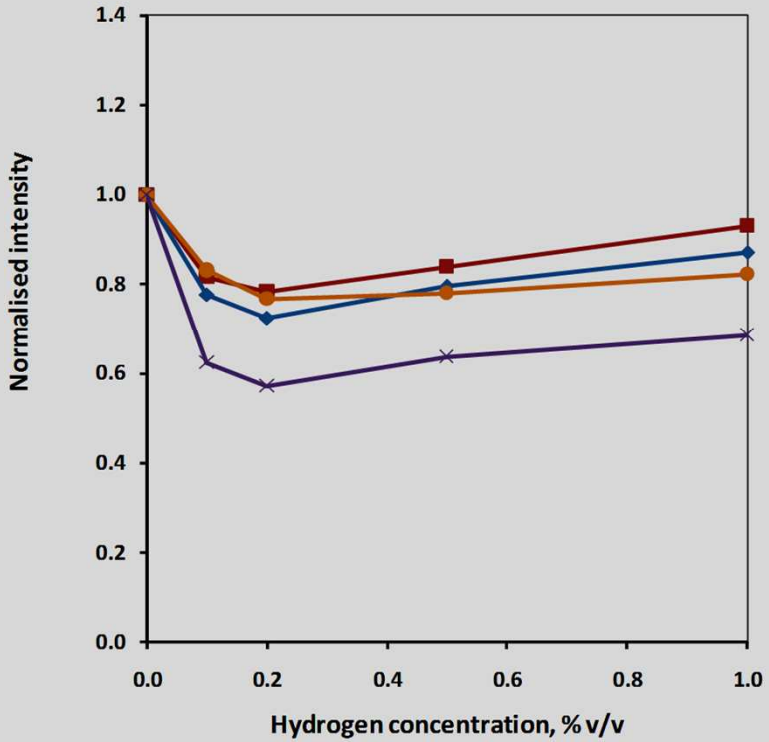
Penning Ionisation

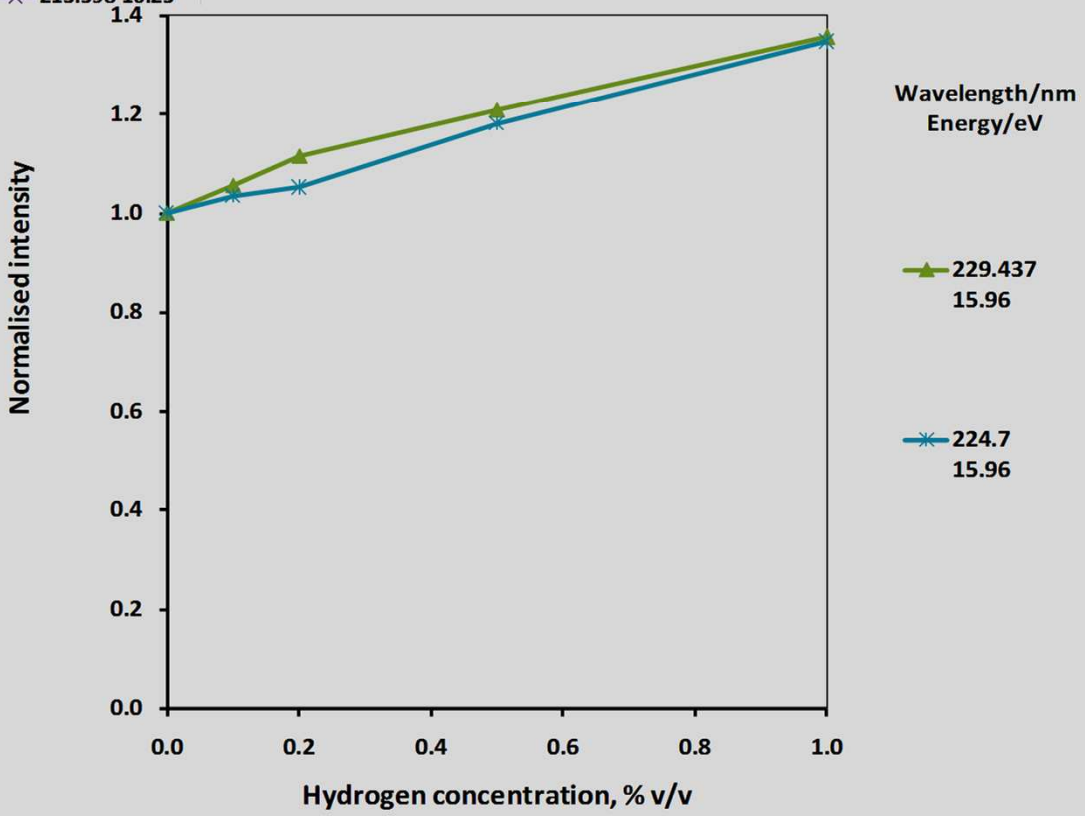
$$G_m + M \Rightarrow G_o + M^{+*} + e + \Delta E$$

NON-RESONANT

where G represents gas. Ar, Ne.....; M sample species Cu. Fe .....
* an excited state, $_m$ a metastable state and $_o$ the ground state.


CT
Ne+
Ne+0
Cu II
Ne I
Nem
PI
CT + cascade
PI
EI
H*2 vib
Cu+0
Cu I
EI
Cu0
Ne0
Energy (eV)
0
2
4
6
8
10
12
14
16
18
20
22


Normalised intensity
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
Hydrogen concentration, % v/v
Wavelength/nm
Energy/eV
221.811 16.15
219.227 16.22
224.261 16.51
213.598 16.25


Normalised intensity
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
Hydrogen concentration, % v/v
Wavelength/nm
Energy/eV
229.437
15.96
224.7
15.96

Attractive explanation – some levels excited by cascade from C T excited levels – the contribution depends on the intensity of the line involved, also zero for some lines, and then increasing Penning Ionisation as hydrogen content increases!

BUT

Attractive explanation – some levels excited by cascade from C T excited levels – the contribution depends on the intensity of the line involved, also zero for some lines, and then increasing Penning Ionisation as hydrogen content increases!

BUT

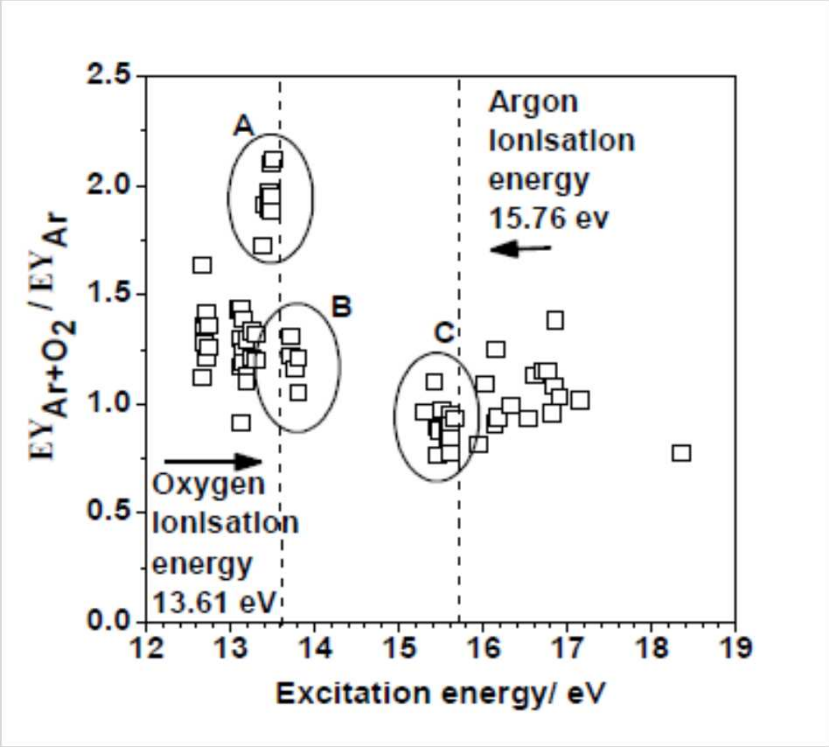
Looking at the self reversal of neon lines, the neon metastable population FALLS with increasing hydrogen concentration.

ADDED OXYGEN (Sohail Mushtaq)

Similar treatment to added hydrogen

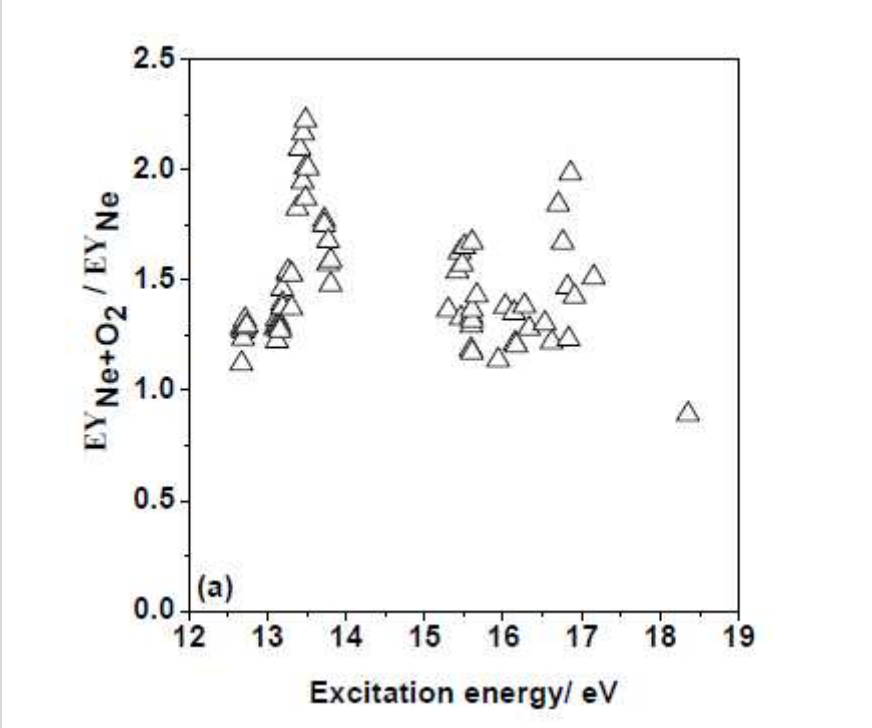
Two approaches – plot against upper energy level for fixed oxygen content,
OR plot intensity of individual lines against oxygen concentration.

ACT by the added gas –
5 years ago, paper by Petr Smid and Steers on H-ACT. - selectiive excitation at 13.6 eV.
Sohail has observed O-ACT also at 13.6 eV. Most obvious in Neon



Oxygen added to argon;
iron sample

Oxygen added to neon.(iron sample)
Note the ACT by oxygen ionic metastable state at 16.9 eV.



MASS SPECTROMETRY!

Ions detected in Mass Spectrometer.

Light emitted by source (have not considered spatial distribution)

Measurements by Viktoria Weinstein with Thermo Element GD, first at EAG Toulouse (Shiva Technology Europe) and then in Syracuse.

Survey with Cu, Fe, Ti samples, added H_2, O_2 and N_2

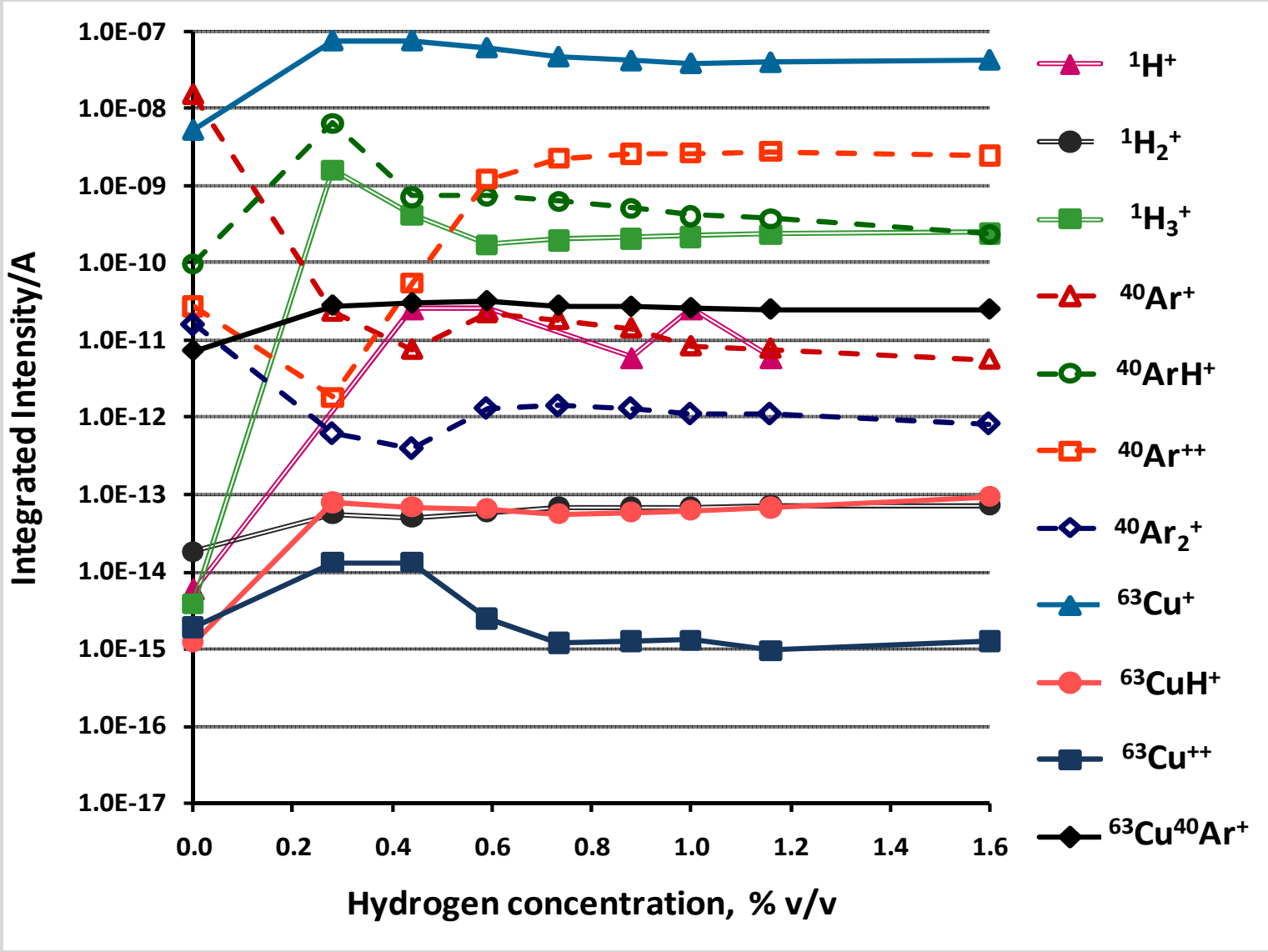
Measurements by Sohail Mushtaq with GD-ToFMS at EMPA. .

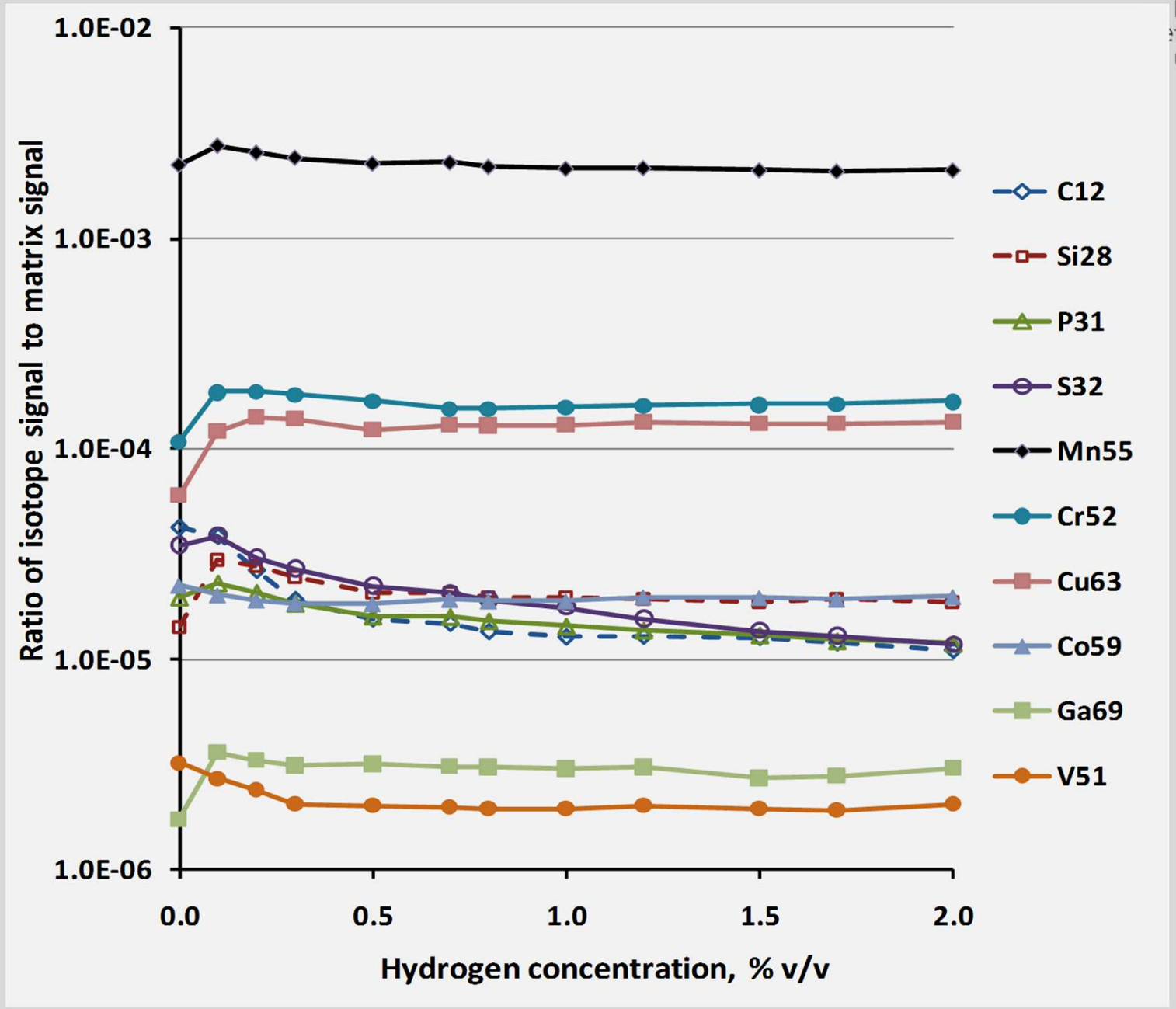
Various samples with added O_2 (H_2 still to be fully evaluated)

Also the negative ion spectrum.

Viktoria's results summarised in poster:
Sohail's in general agreement.
What about used neon????

LONDON metropolitan university




1.0E-02
1.0E-03
1.0E-04
1.0E-05
1.0E-06
Ratio of isotope signal to matrix signal
0.0
0.5
1.0
1.5
2.0
Hydrogen concentration, % v/v
C12
Si28
P31
S32
Mn55
Cr52
Cu63
Co59
Ga69
V51

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.

Magnitude of the effects differ with discharge conditions.

The majority of the effects occur at molecular gas concentration higher than those occurring in analytical practice.

Ich danke Ihnen für Ihre Aufmerksamkeit