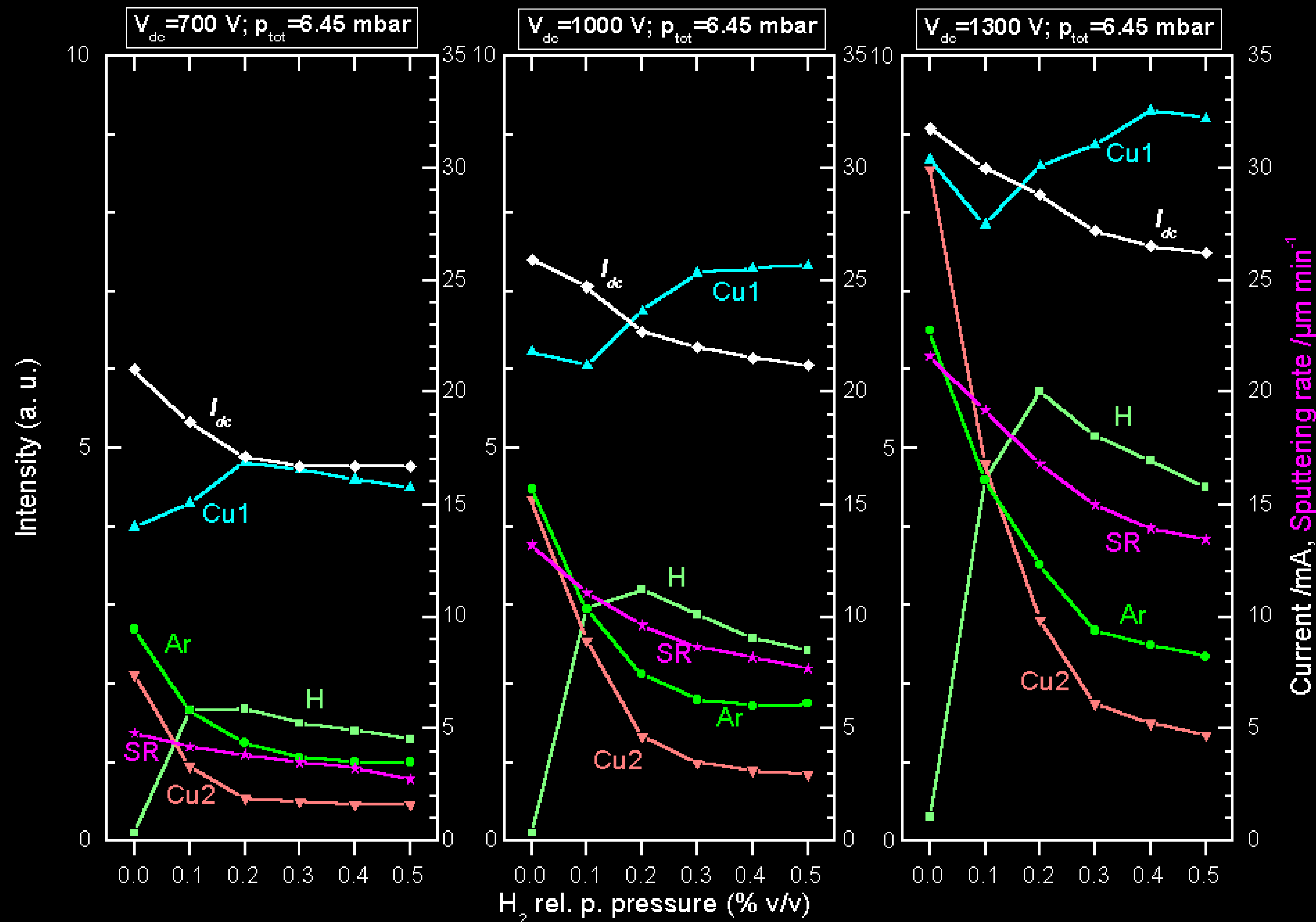
Einfluss der molekularen Gase (N_2,H_2) auf die Fe I und Ti I Spektren

E. Steers und P. Šmíd
(London Metropolitan University, UK)

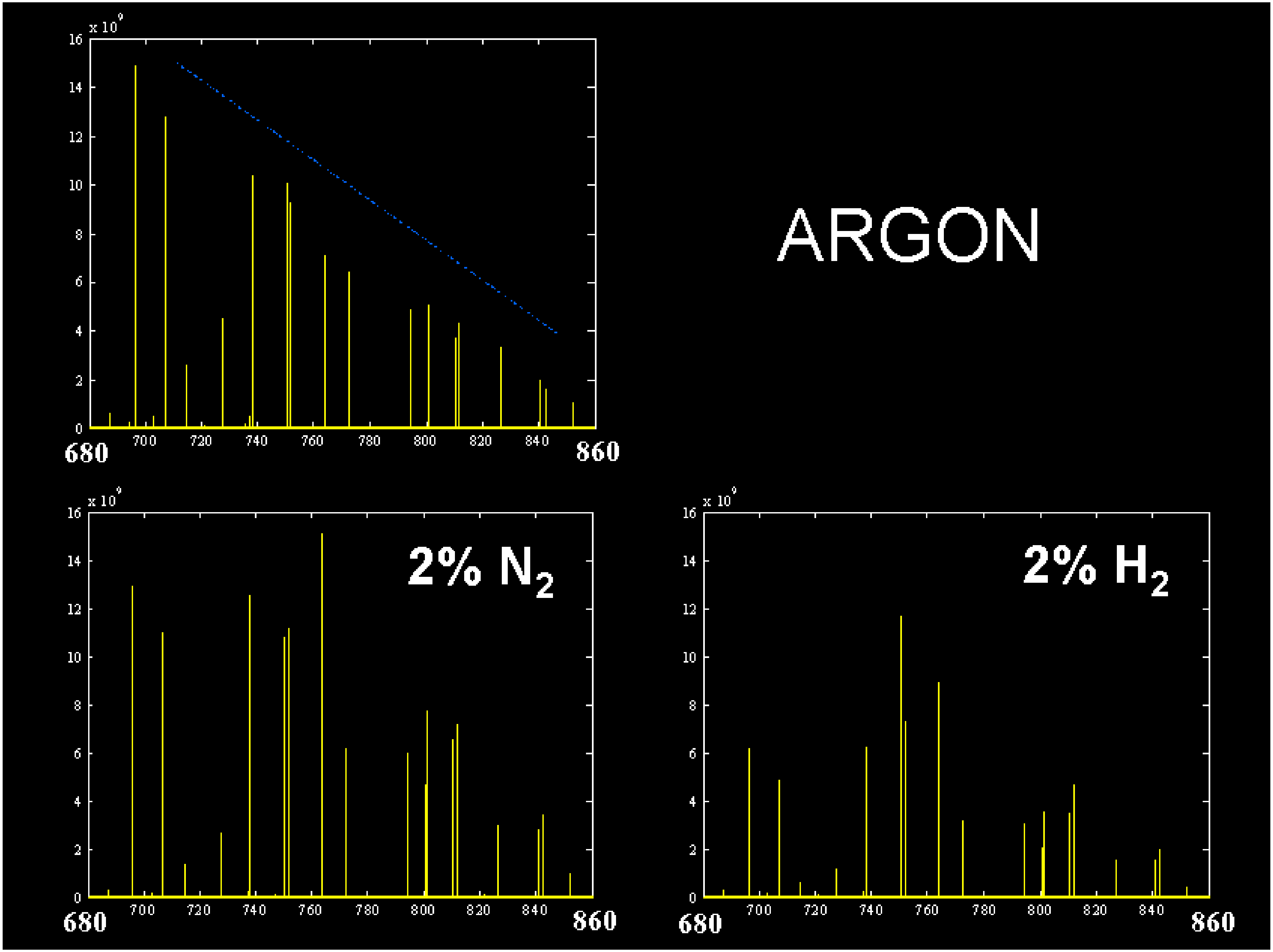
Introduction

- Effect of molecular gases (H_2, N_2 and O_2) on analytical glow discharges has been studied intensively for the last decade
- Molecular gases affect electrical characteristics, sputtering rate, optical emission in GD-OES and ionic signal in GD-MS $\Rightarrow$ analytical results can be incorrect
- H comes from residual moisture
- Hydrocarbons produced by rotary pumps
- N can be present as a residual gas in the source or come from a leakage
- Both elements can be present in the sample

Authors	Gases	Range	Approach
Fischer	N_2, O_2		
Bengtson	H_2		Behaviour of Cr lines
Hodoroaba	H_2	0, 0.05 – 2%	Many Cu and Ar lines; one line from several elements
Oviedo Group	H_2, N_2, O_2	0, 0.5 – 10%	one line from several elements
Šmíd (PhD work)	N_2	0, 0.02 – 2%	Many lines of Fe, Ti and Ar
Steers, Šmíd & Weiss	N_2, H_2	0, 0.02 – 2%	Many lines of Fe, Ti. Ar & Ne etc
Cvetanovic		? – 3%	10 Ti I lines
Köster	H_2		Line enhancement for analysis

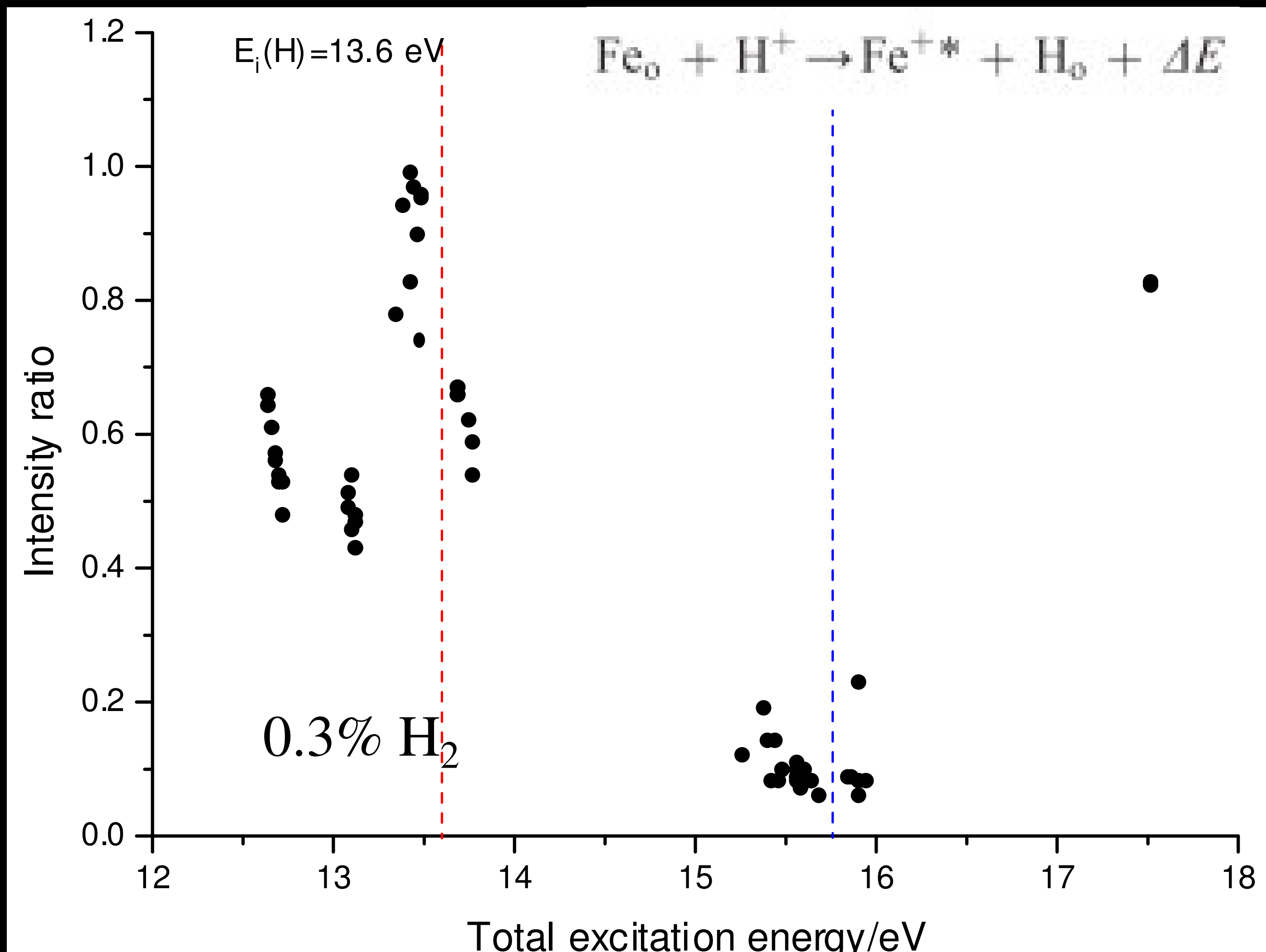


V-D.Hodoroaba, thesis



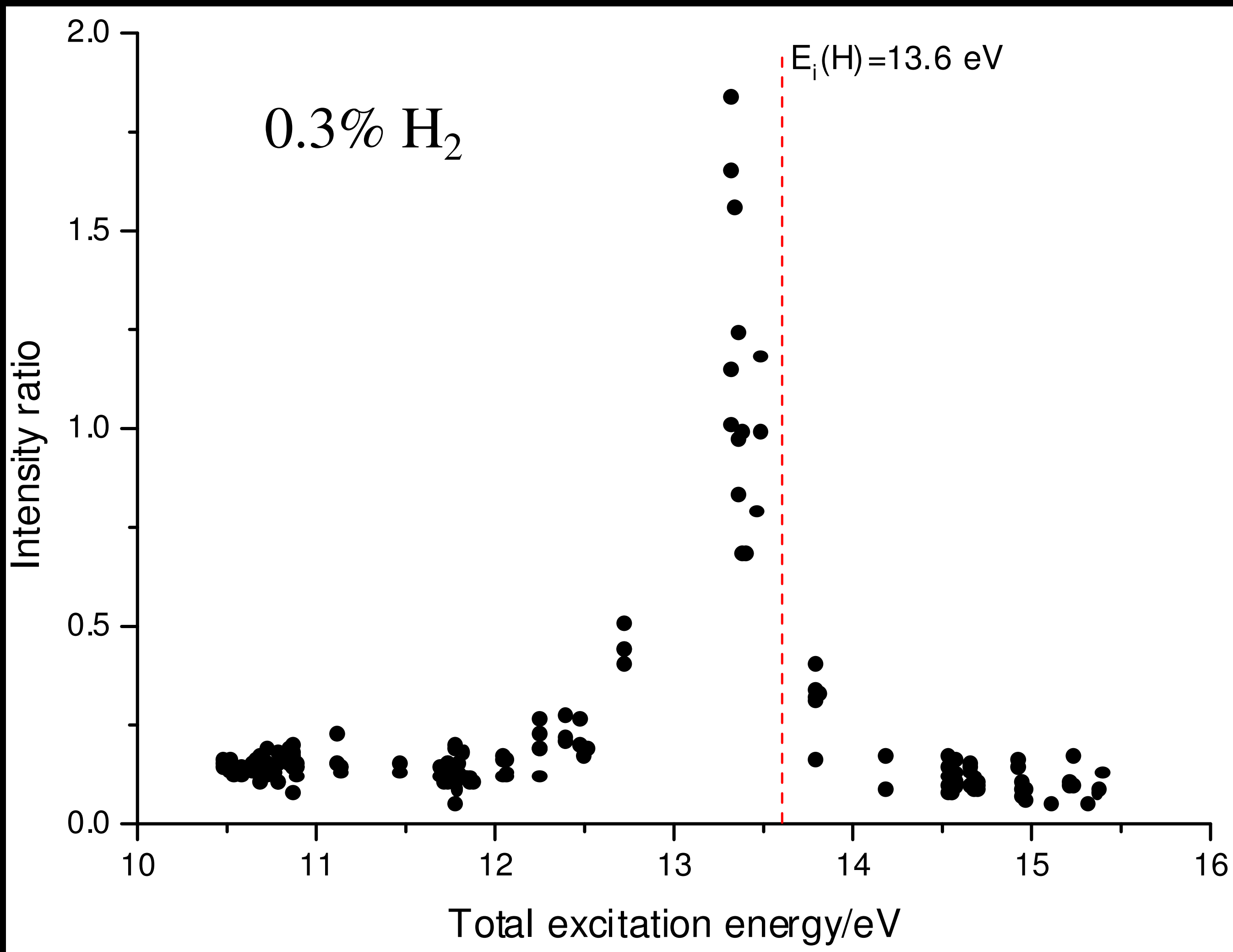
ARGON
2% N2
2% H2
x 10^9
16
14
12
10
8
6
4
2
0
680
700
720
740
760
780
800
820
840
860

Results – Fe II



E. B.M. Steers, P. Šmíd and Z. Weiss, Spectrochim. Acta Part B, 2006, 61, 414–420

Results – Ti II lines



E. B.M. Steers, P. Šmíd and Z. Weiss, Spectrochim. Acta Part B, 2006, 61, 414–420

Experimental – **IC London**

- Standard Grimm-type source with 4 mm anode tube
- Gases: Ar mixed with a premixed gas ($Ar+2\%H_2$ or $Ar+2\%N_2$) using a mixing system with MKS MFCs
- Electrical excitation:
  - dc with current stabilized dc power supply – constant V&i
- Vacuum uv FTS instrument:
  - Spectral range: 135-900 nm
  - Limit of resolution 0.035 cm^{-1} $\Rightarrow$ chromatic resolving power $1.4x10^6$ and a resolution of 0.14 pm at 200 nm
  - Detection: PMT
- Advantages:
  - Wide spectral range at high resolution in rel. short acquisition times (a few minutes)
  - Accurate wavelength determination

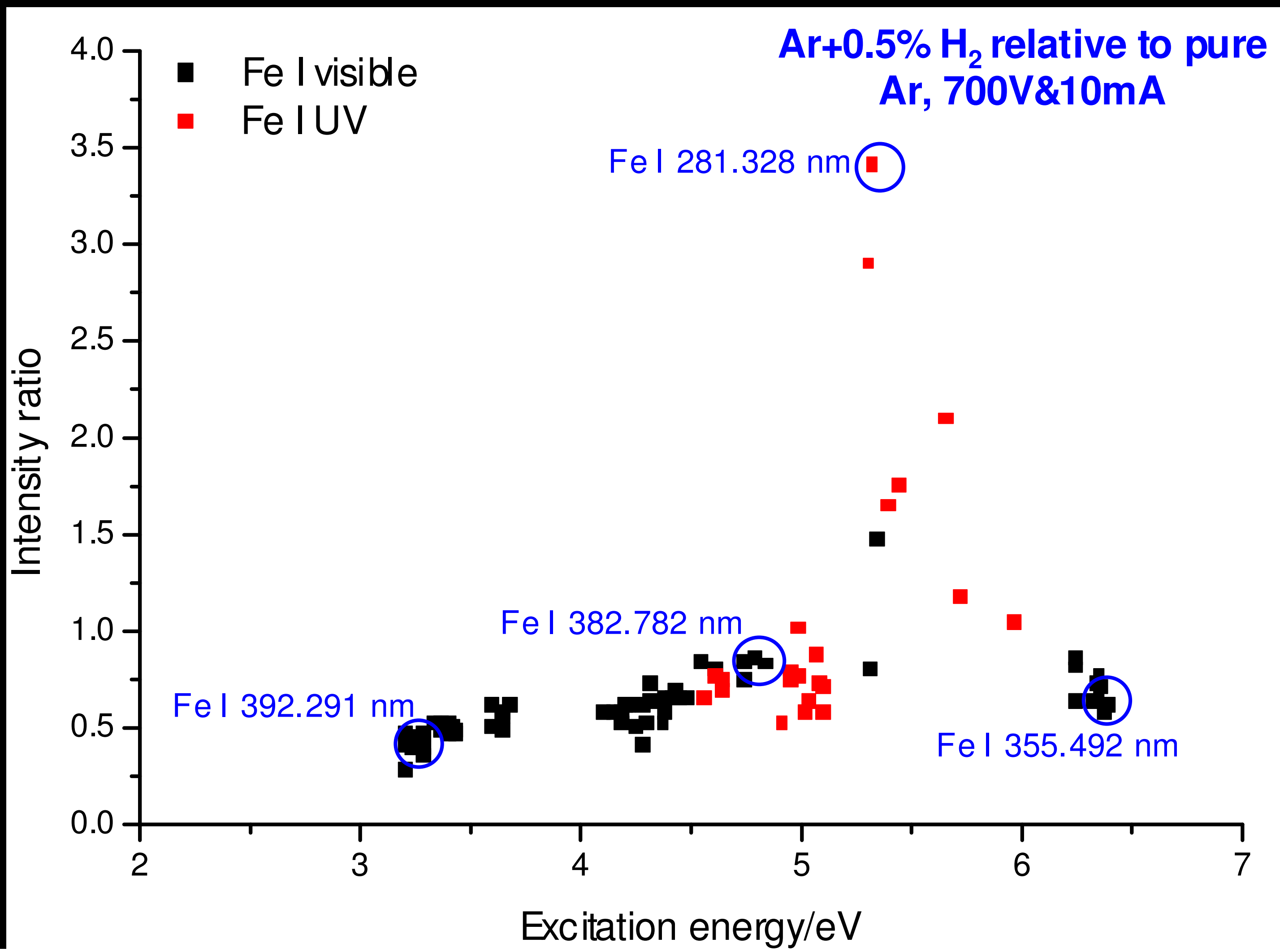
Experimental – **IFW Dresden**

- Standard Grimm-type source with 4 mm anode tube and integrated voltage and current probes for rf measurements
- Gases: Ar mixed with a premixed gas (Ar+2%H_2 or Ar+2%N_2) using a mixing system with Bronkhorst MFCs
- Electrical excitation:
  - rf with free running generator (3.4 MHz) – constant P&V_{rms}
  - dc, const V and I
- Echelle CCD spectrometer LLA ESA 3000
  - Spectral range: 200-1000 nm
  - Resolution: 5 pm at 200 nm, 27 pm at 600 nm
  - Detection: ICCD
- Advantages:
  - Rapid acquisition of spectra at high resolution (a few seconds)

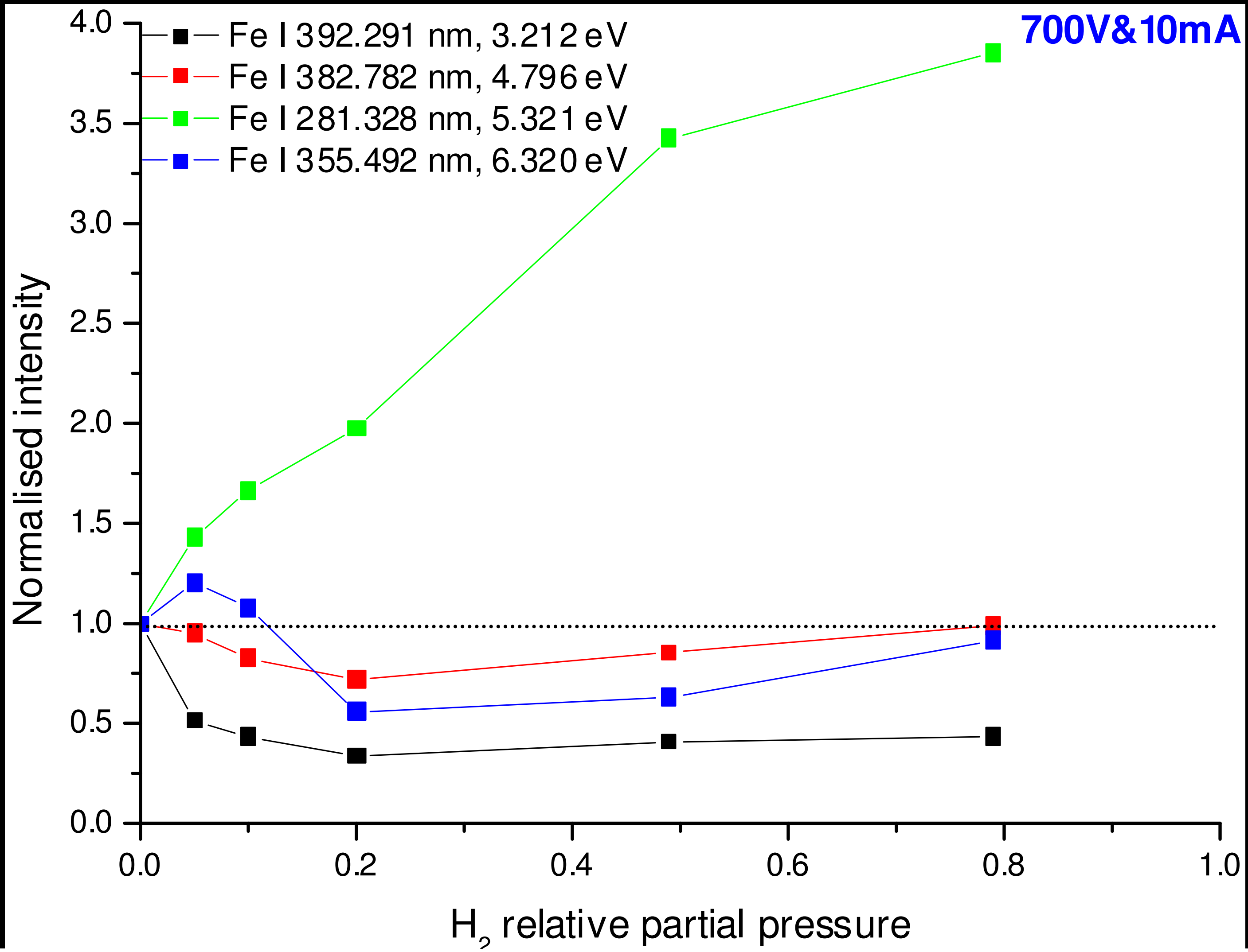
Experimental

- Comparison of spectra of pure **Fe** and **Ti** recorded in pure argon and argon with various hydrogen or nitrogen concentrations
- Running in modes with const. V and const. I (dc), and const. P and const. V_{rms} (rf)
- Spectra recorded over wide wavelength range:
  - 200-300 nm (UV)
  - 300-600 nm (“visible”)
- Line identification and selection – unambiguous identification, sufficient intensity, free of interferences and reliable data on energy levels:
  - Fe I lines – 97 lines, Fe II lines – 82
  - Ti I lines – 129 lines, Ti II lines – 192

Results – Fe I lines

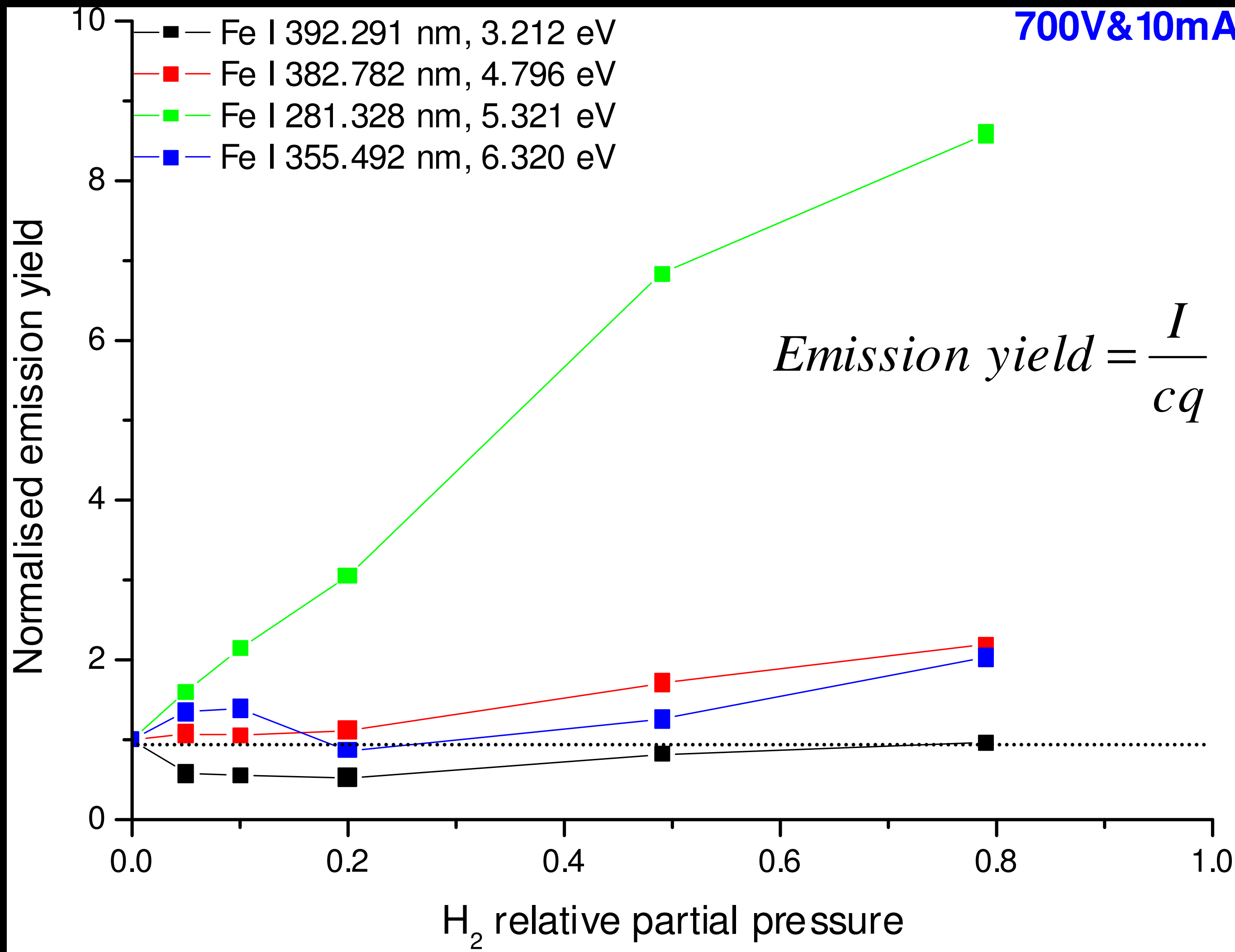


Results – Fe I lines



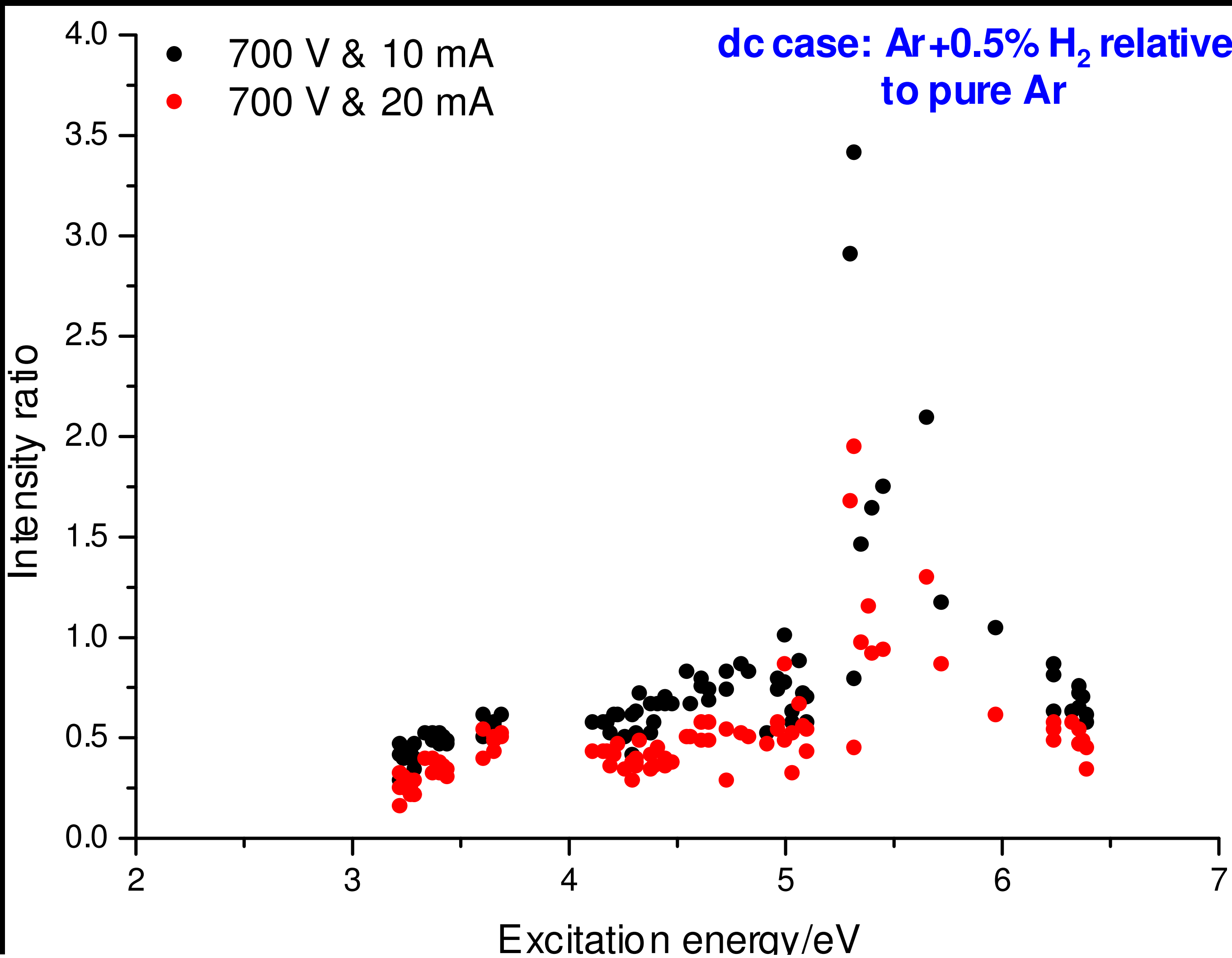
Results – Fe I lines

Emission Yield!

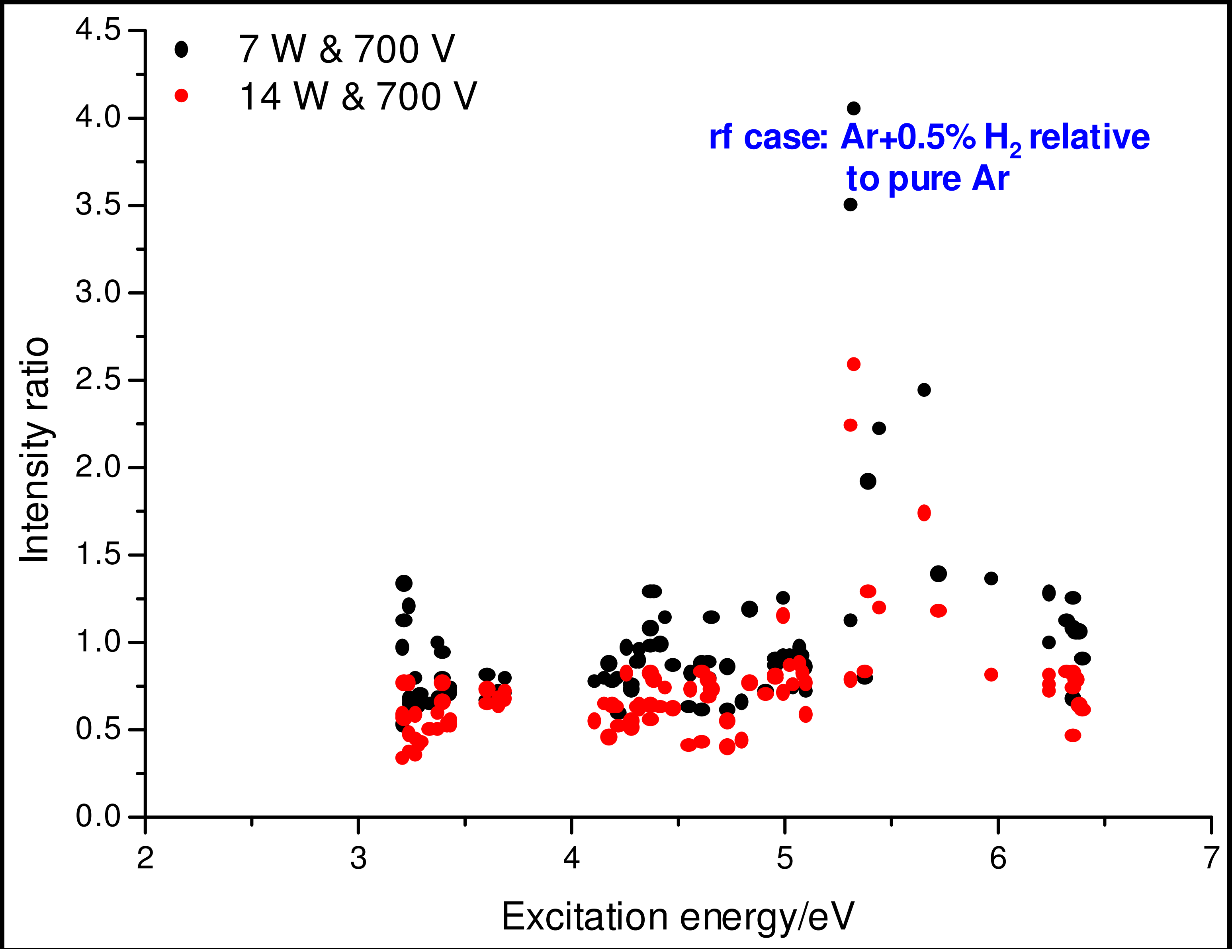


Results – Fe I lines

Effect of current

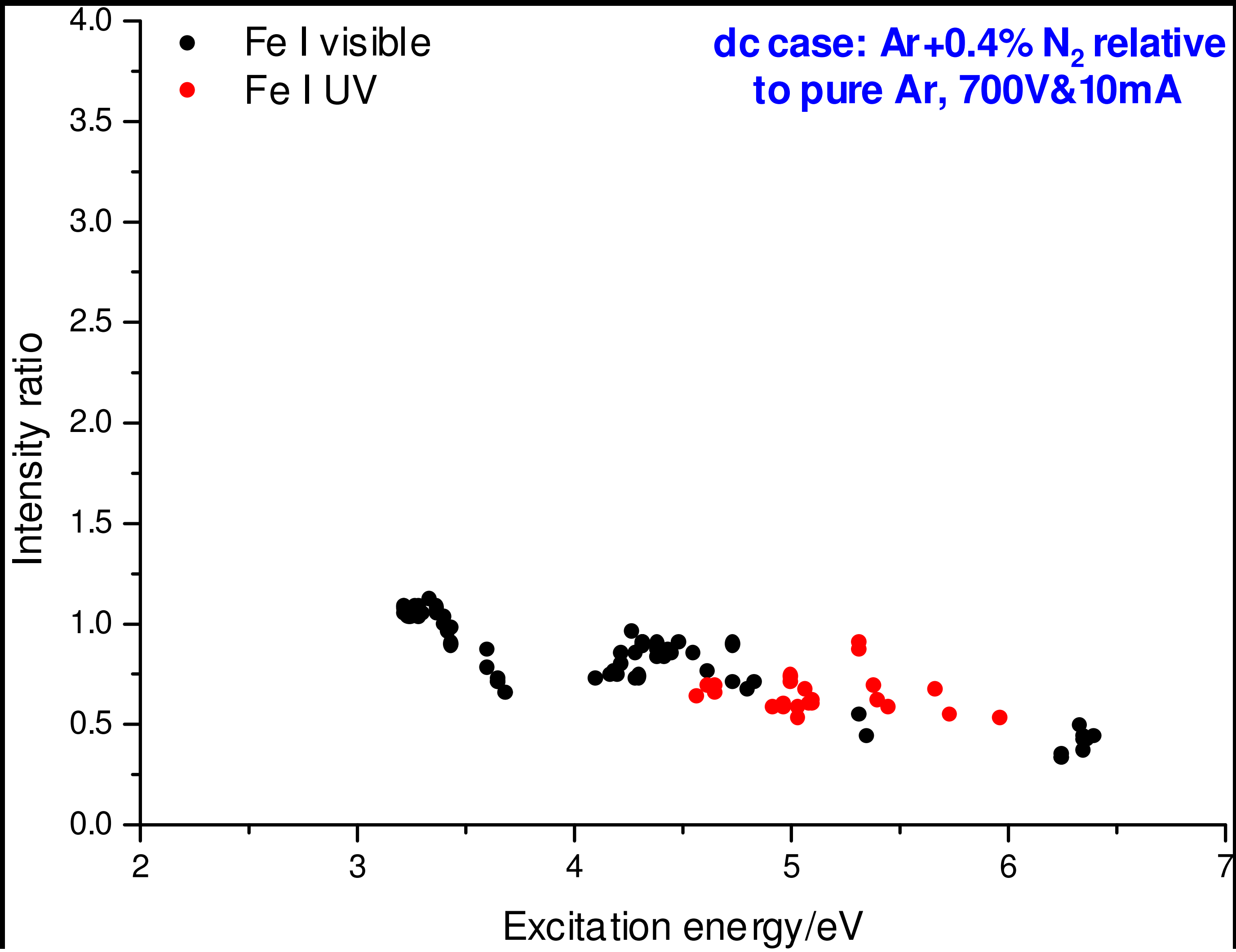


Results – Fe I lines

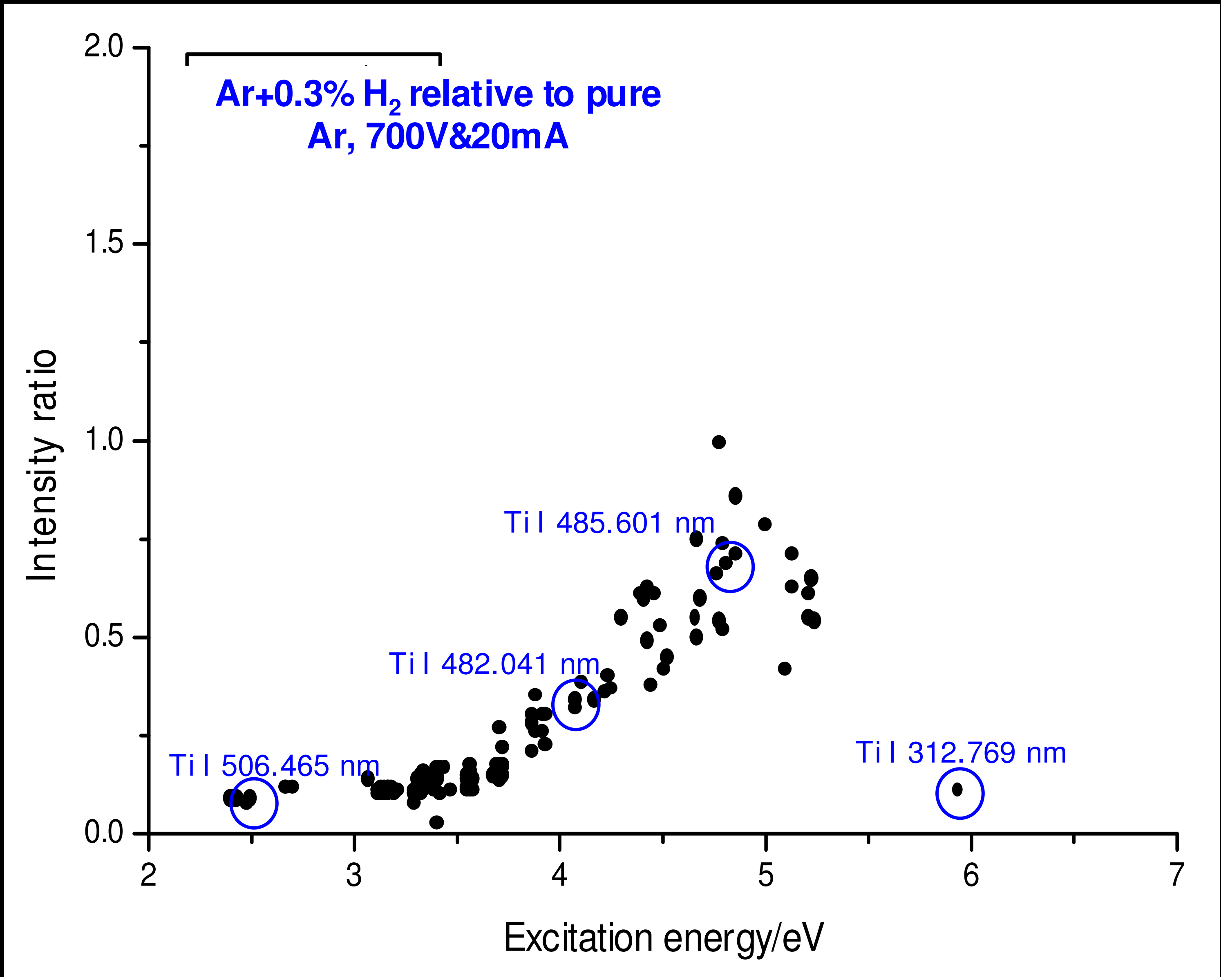


Results – Fe I lines

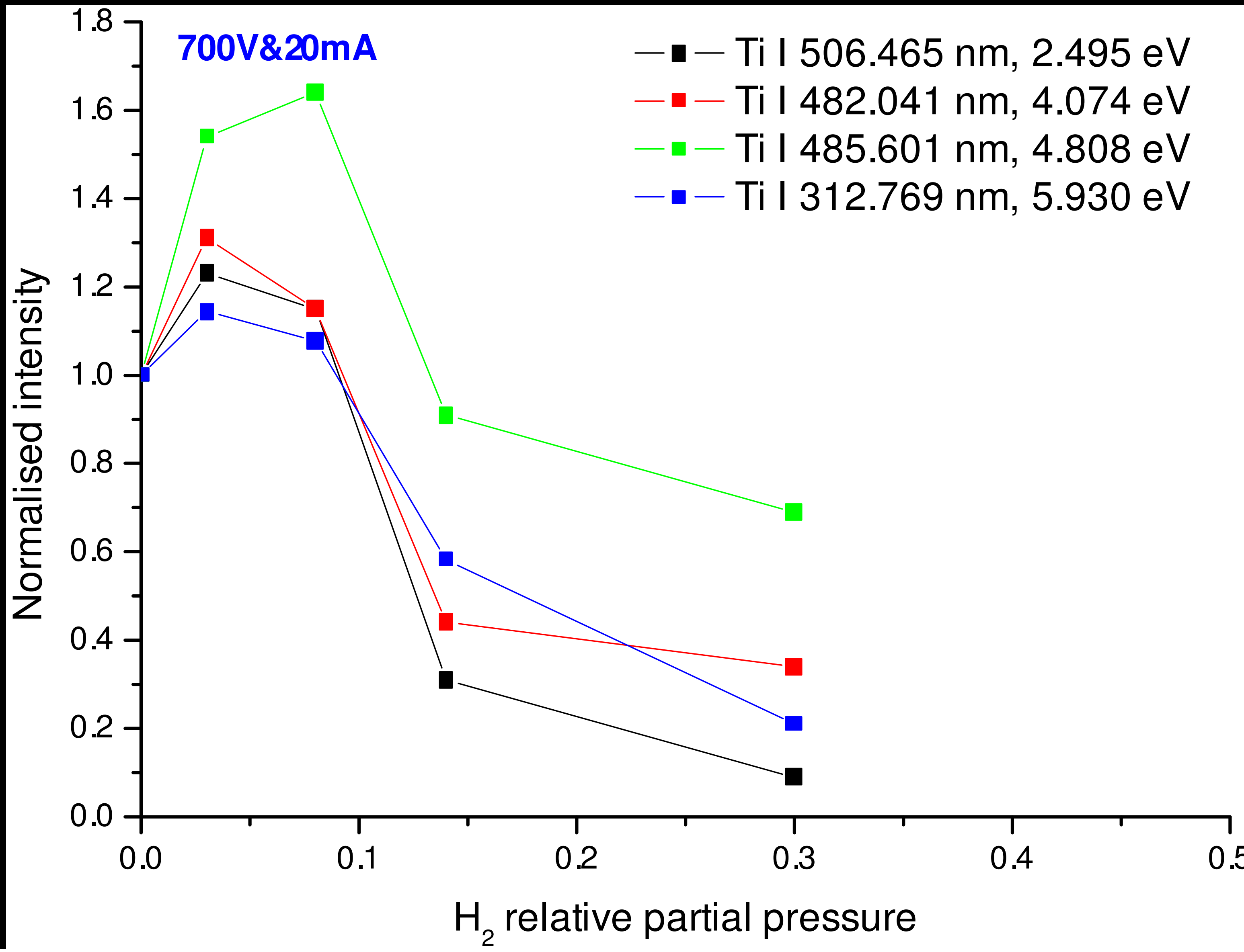
Effect 0f Nitrogen



Results – Ti I lines

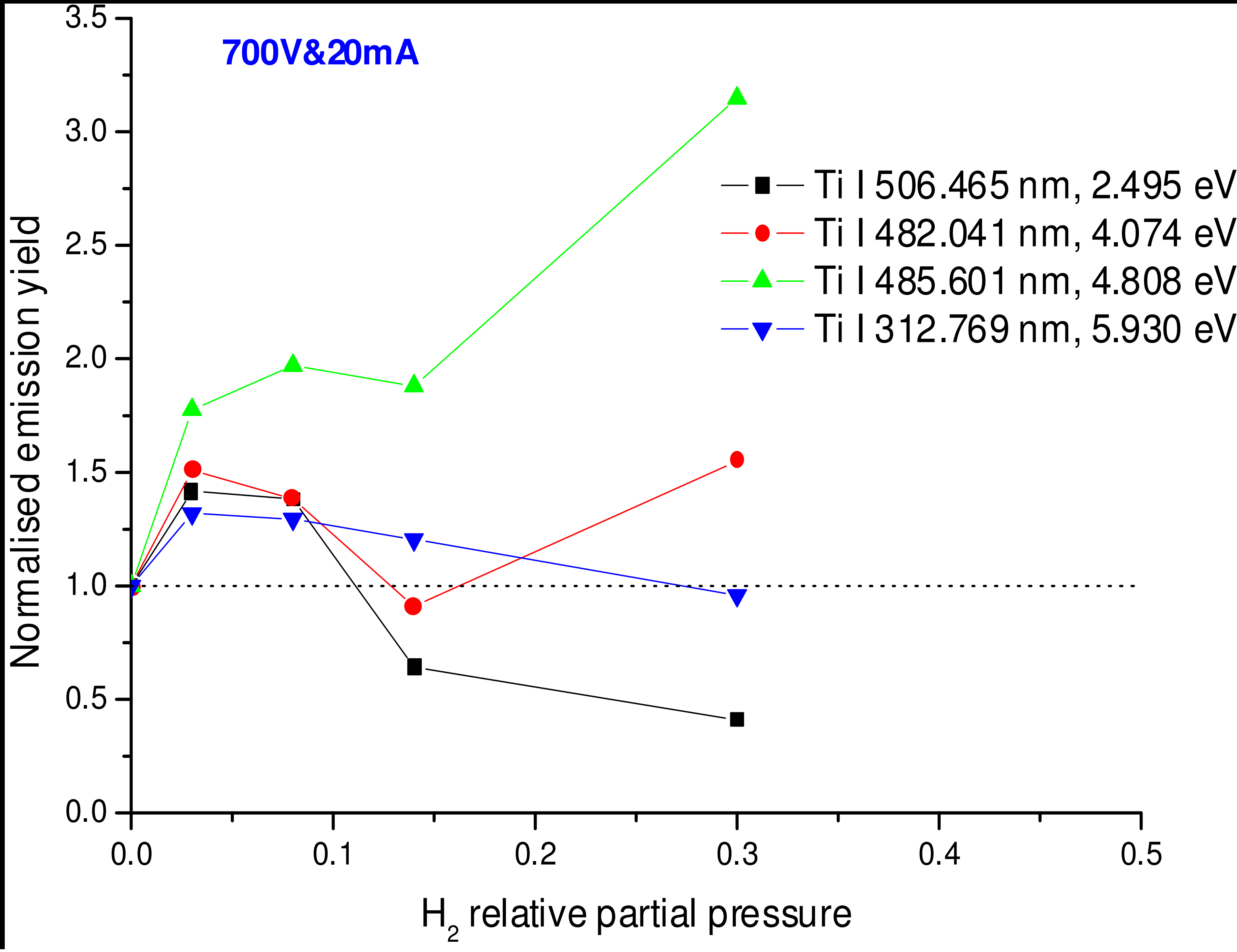


Results – Ti I lines

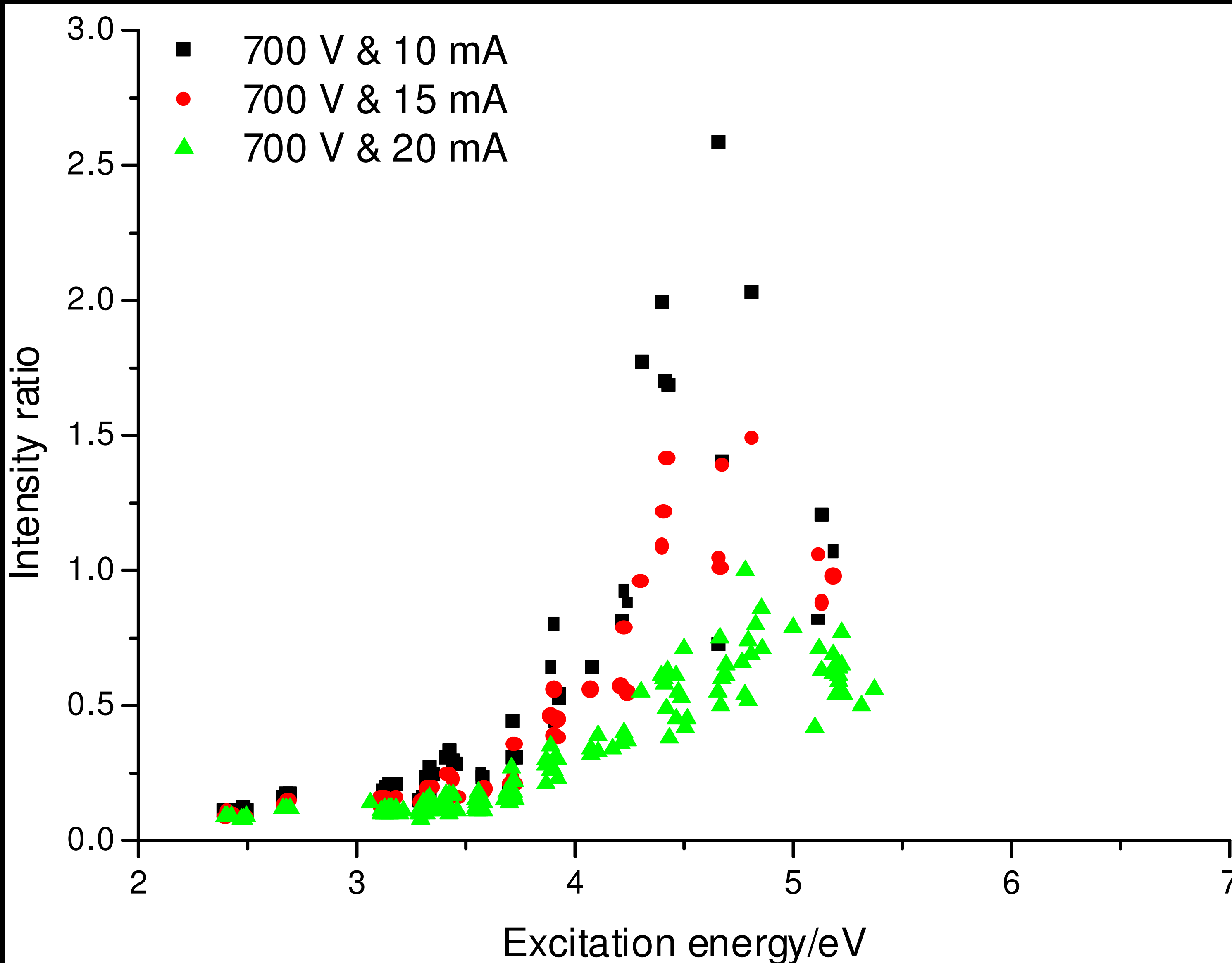


Results – Ti I lines

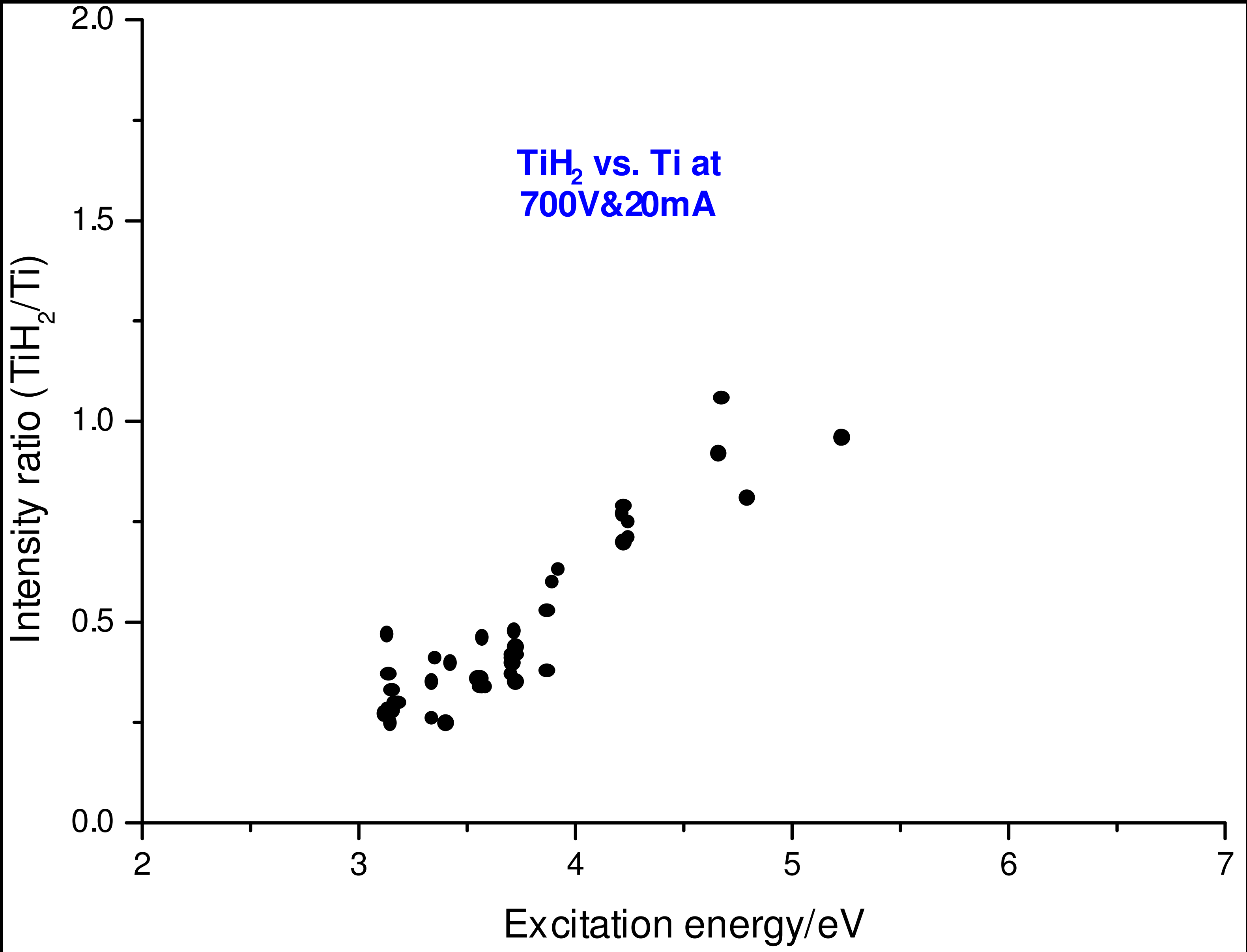
Emission Yield!

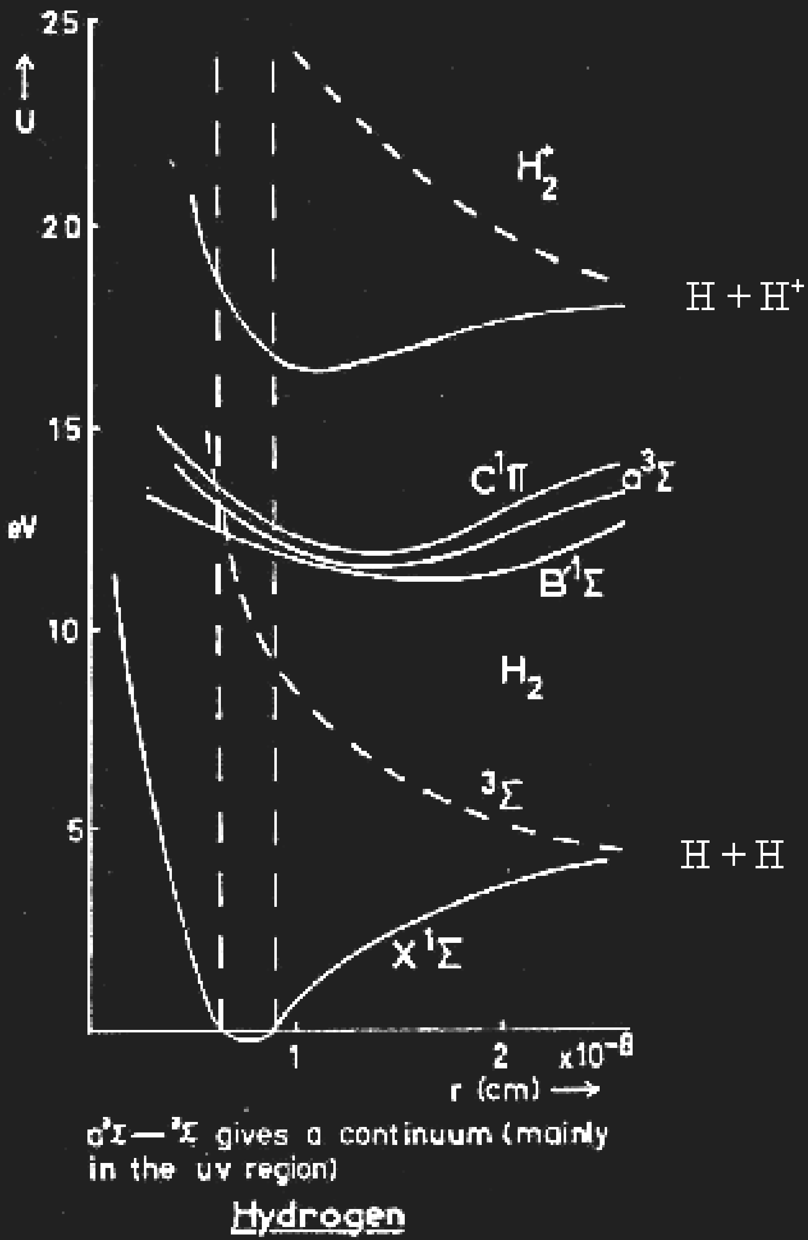


Results – Ti I lines



Results – Ti I lines



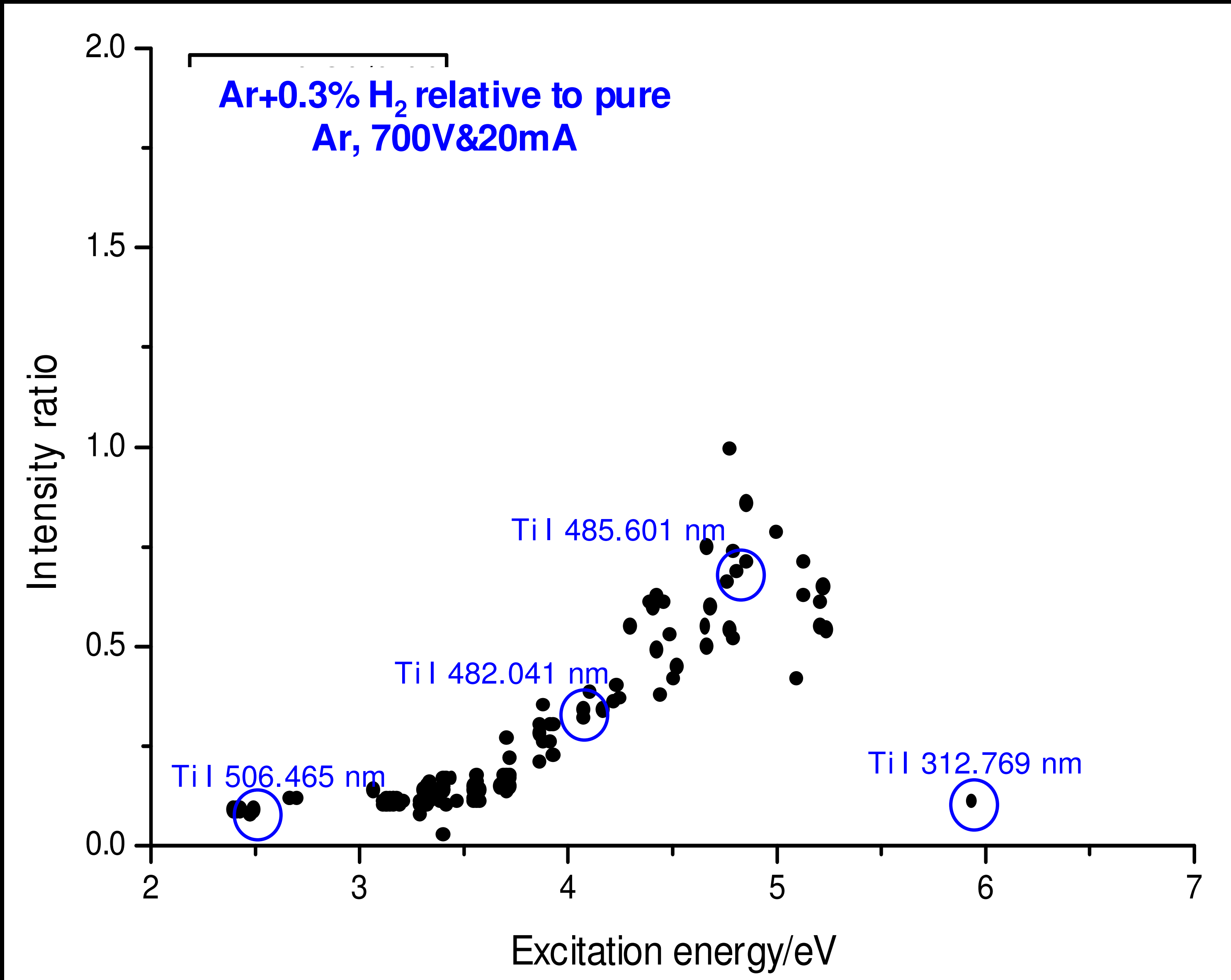


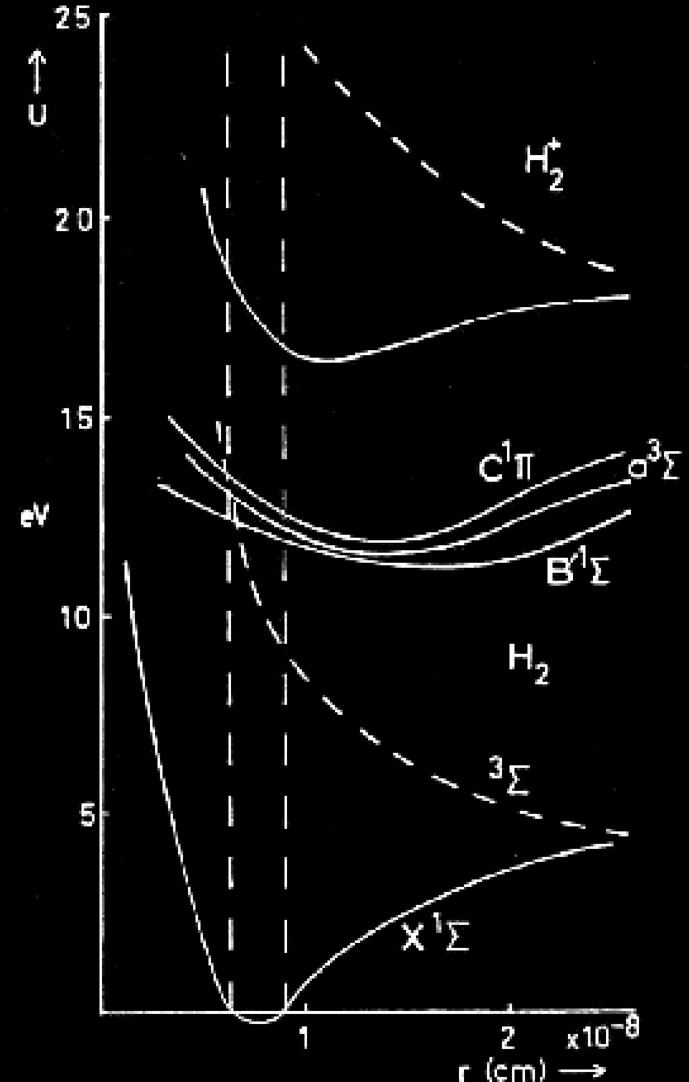
A possible explanation!

$M + H_2^+ \rightarrow H + H^+ + M^*$

Three products, so do not require an exact energy resonance to satisfy collision parameters

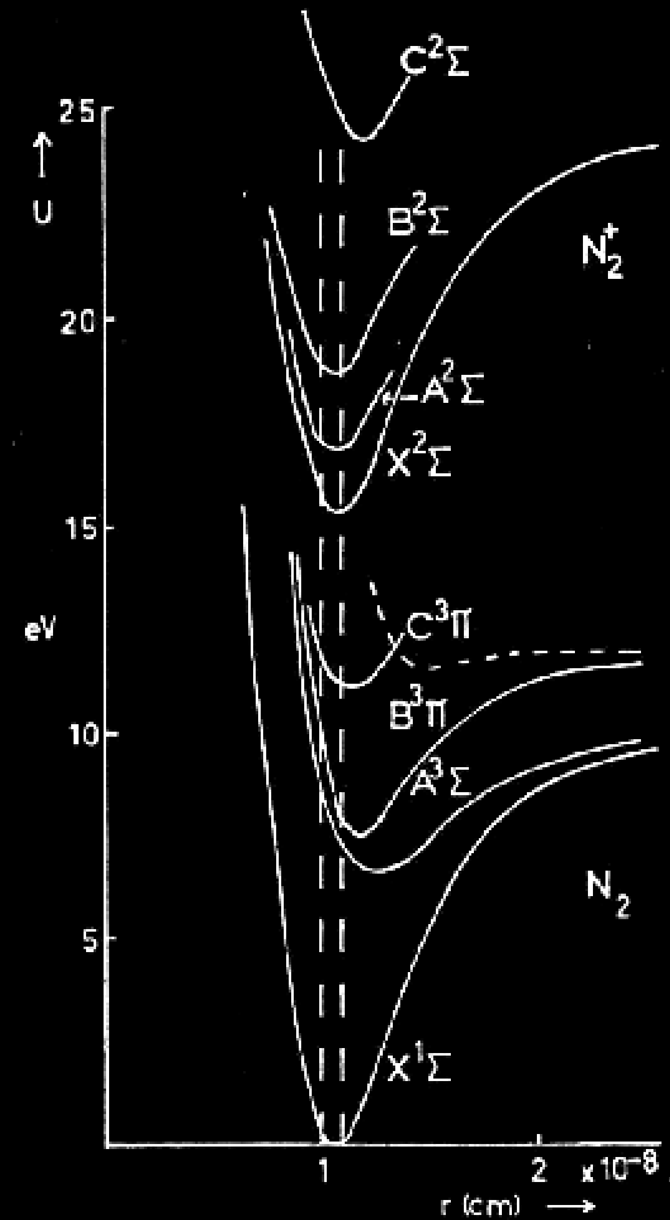
Results – Ti I lines





$a^3\Sigma$ — $^3\Sigma$ gives a continuum (mainly in the uv region)

Hydrogen



Nitrogen

Conclusions

- The effect of hydrogen on large number of Fe I and Ti I emission lines has been described.
- Correlation between the intensity ratios and the excitation energy has been found.
- In case of Fe I lines, strong enhancement has been observed for the lines with excitation energy between 5.3 and 5.6 eV.
- This enhancement is stronger for lower currents
- No such trends has been observed in case of nitrogen.

Ich danke Ihnen für Ihrer Aufmerksamkeit

Es freut mich, Bermerkungen zu bekommen, aber fragen Sie auf Englisch, bitte!