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Non-invasive measurements of plasma parameters via optical emission spectroscopy

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Ann Arbor, MI, December 10, 2014

Acknowledgments

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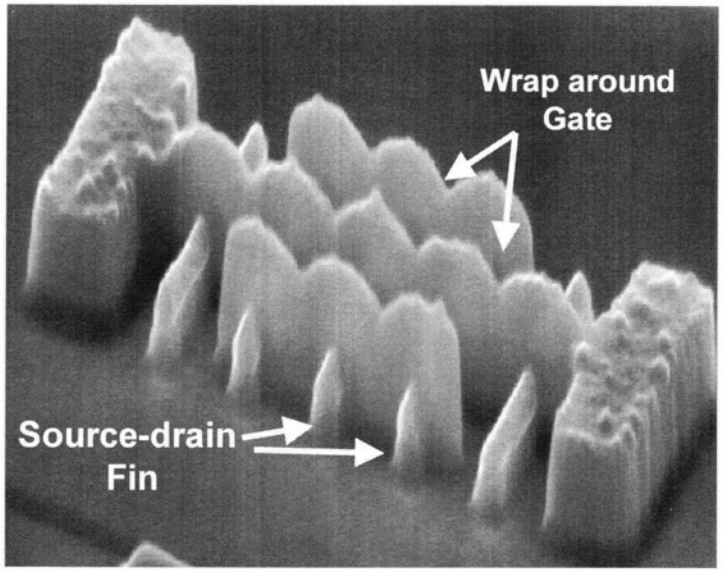
- Collaborators and students
  - Dr. John Boffard, UW Physics Dept.
  - Prof. Chun C. Lin, UW Physics Dept.
  - Shicong Wang, UW ECE Dept.
  - Cody Culver, UW Materials Science Program
  - Nathaniel Ly, UW ECE Dept.
  - Dr. Ryan Jung, UW Physics Dept. (now at IBM)
  - Lauren Aneskavich, UW ECE Dept. (now at Rockwell Automation)
  - Dr. Svetlana Radovanov, Applied Materials Corp.
  - Dr. Harold Persing, Applied Materials Corp.

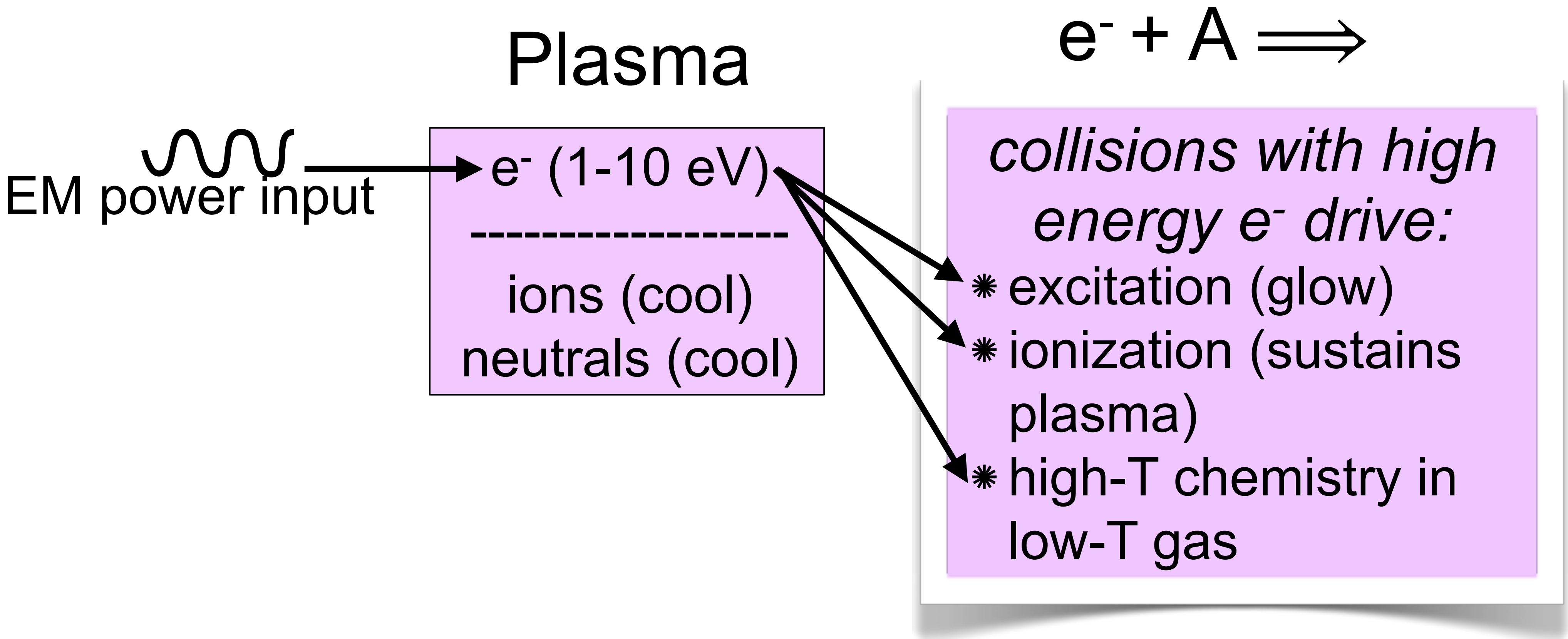
- Support
  - National Science Foundation
  - Applied Materials
  - UW Graduate School/Wisconsin Alumni Research Foundation

Low-temperature plasma applications

- applications are diverse
- manipulating plasma is a means to control technological outcomes
- diagnostic tools are needed to improve plasma science understanding



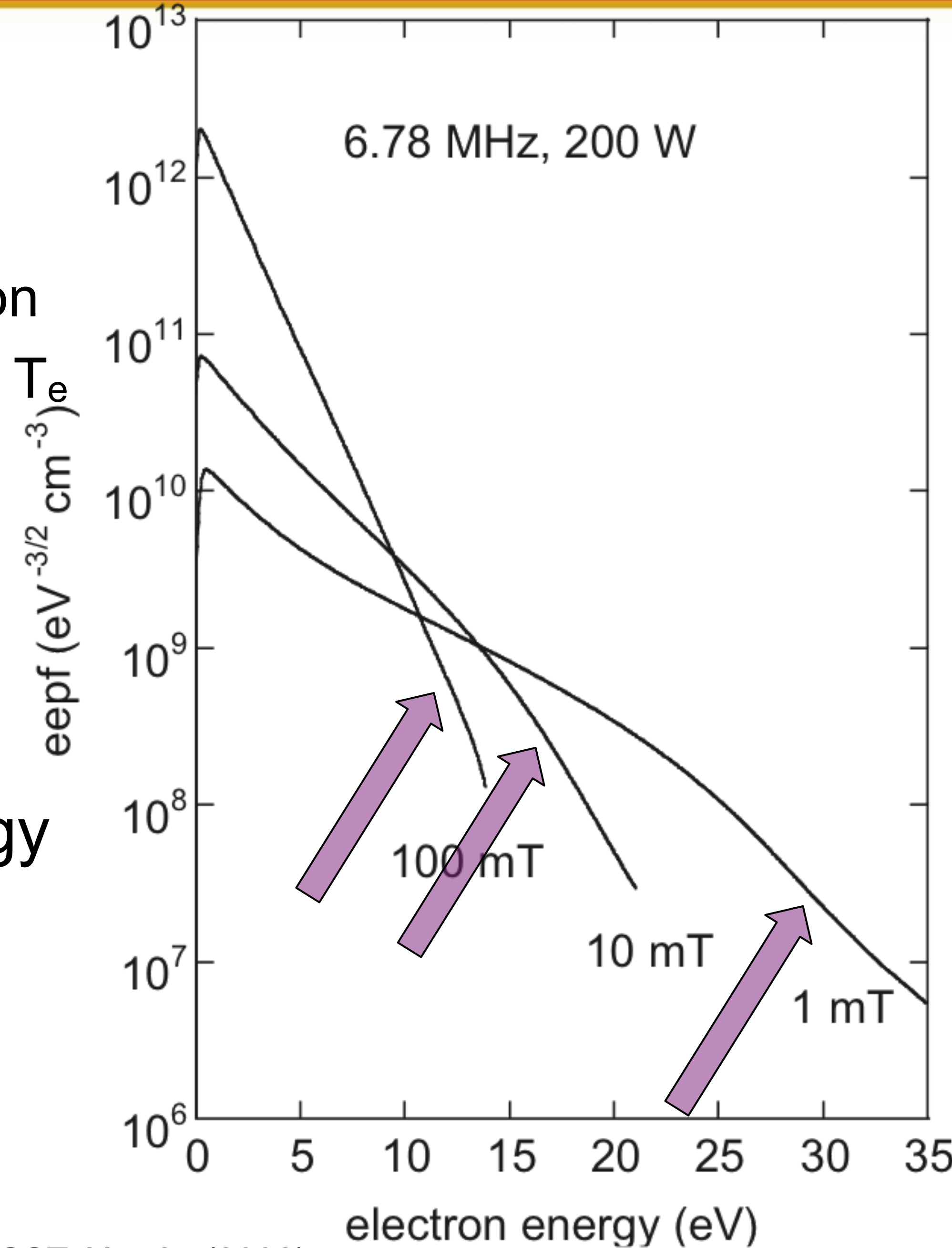
LTPs are non-equilibrium systems



- *energetic electrons are key link in process outcomes*

Electron energy distribution functions

- Maxwellian EEPF appears as straight line -
  - corresponds to thermodynamic equilibrium *within* electron population
  - characterized by single parameter - T_e



- RF inductively coupled plasmas: EEDFs with 'depleted' high energy 'tails'
  - attributed to:
    - inelastic collisions
    - escape to walls

Godyak *et al.*, PSST **11**, 525 (2002)

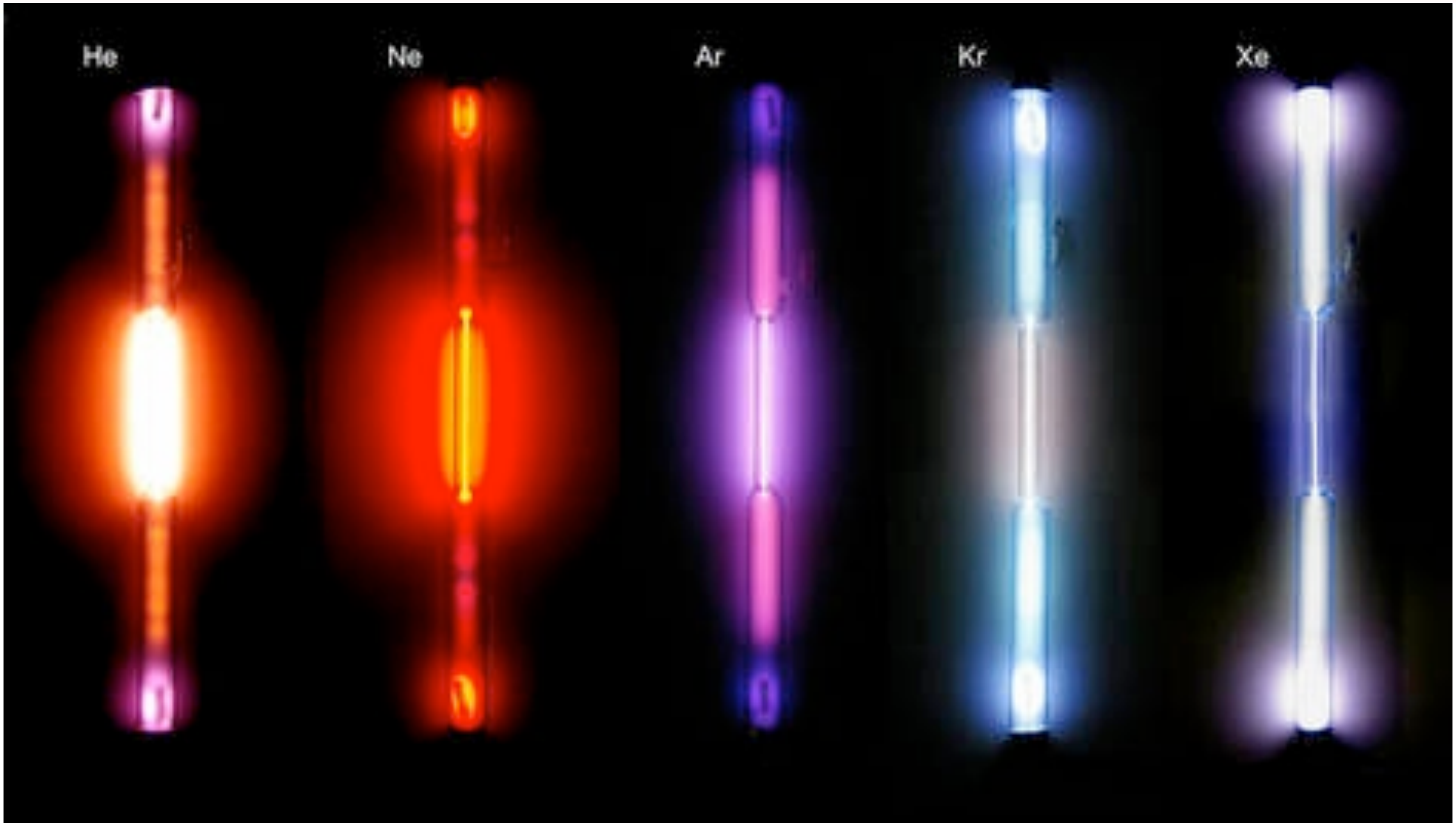
Presentation Outline: Optical diagnostics for plasma characterization

- Optical emission spectroscopy of argon-containing plasmas
  - emission model for determination of
    - EEDF, T_{eff}
    - metastable and resonance level densities
    - electron density - n_e
    - Example: non-Maxwellian EEDFs in inductively coupled plasma

- Real-time plasma monitor
  - metastable and resonance level densities - n_m and n_r
  - effective electron temperature - T_{eff}
  - electron density - n_e

- VUV detection
  - resonance level densities - n_r - as a proxy for Ar VUV flux

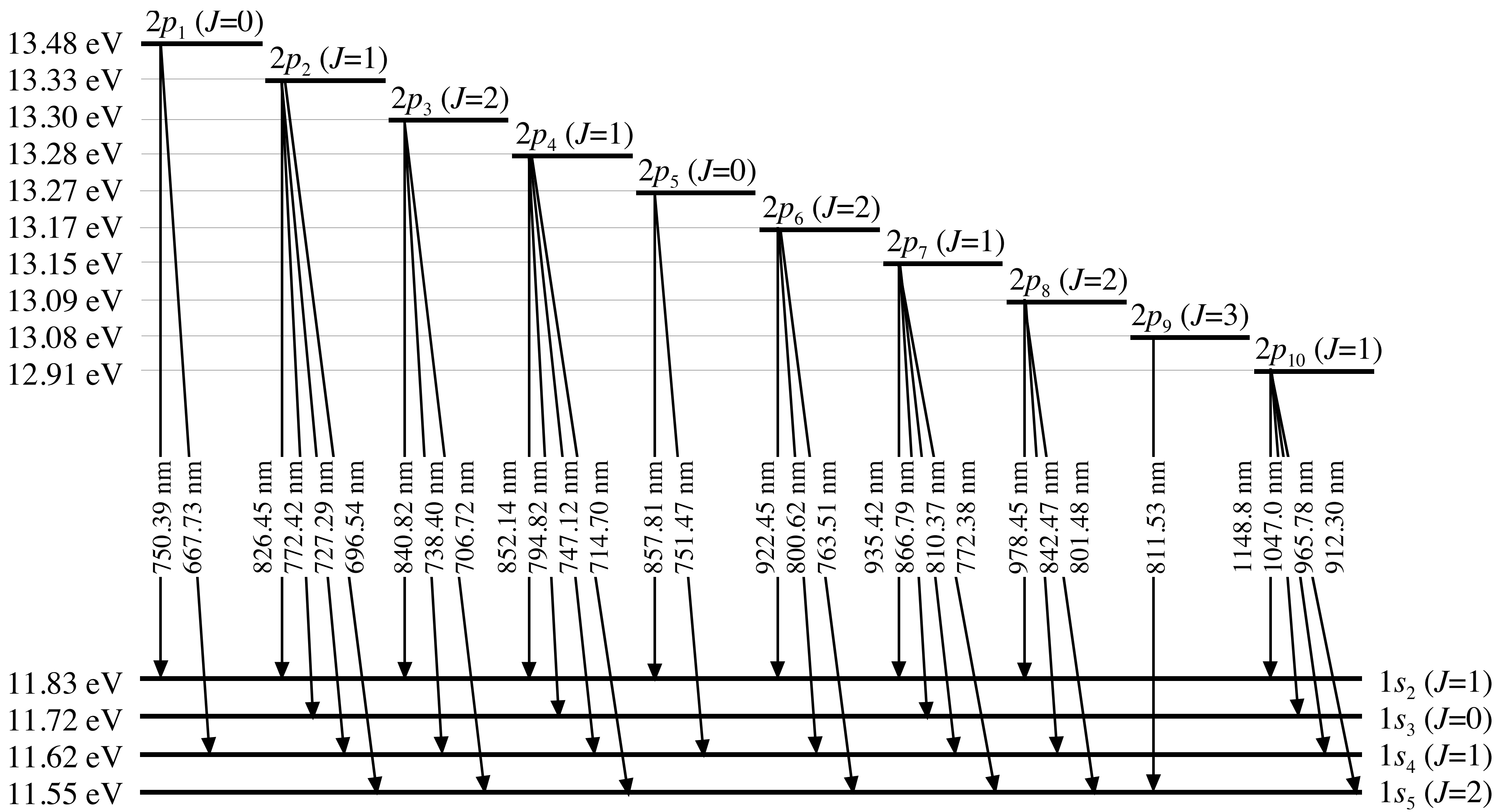
Each plasma emits distinctive spectrum



- http://wapedia.mobi/en/Gas_filled_tube - different rare gases
- Also, plasmas with the *same* gas changes colors with conditions

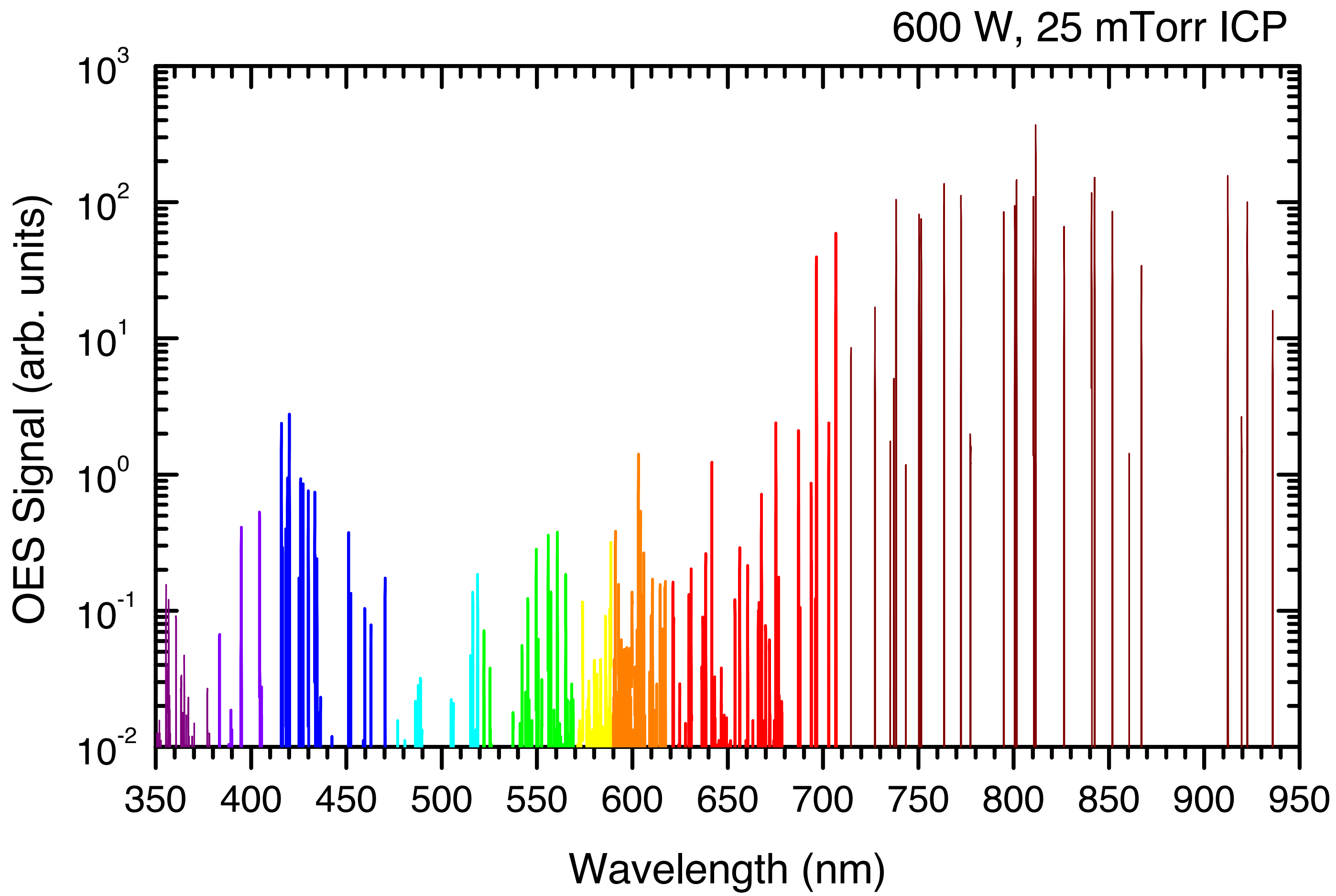
Partial Ar energy level diagram

- Allowed transitions resulting in photon emission



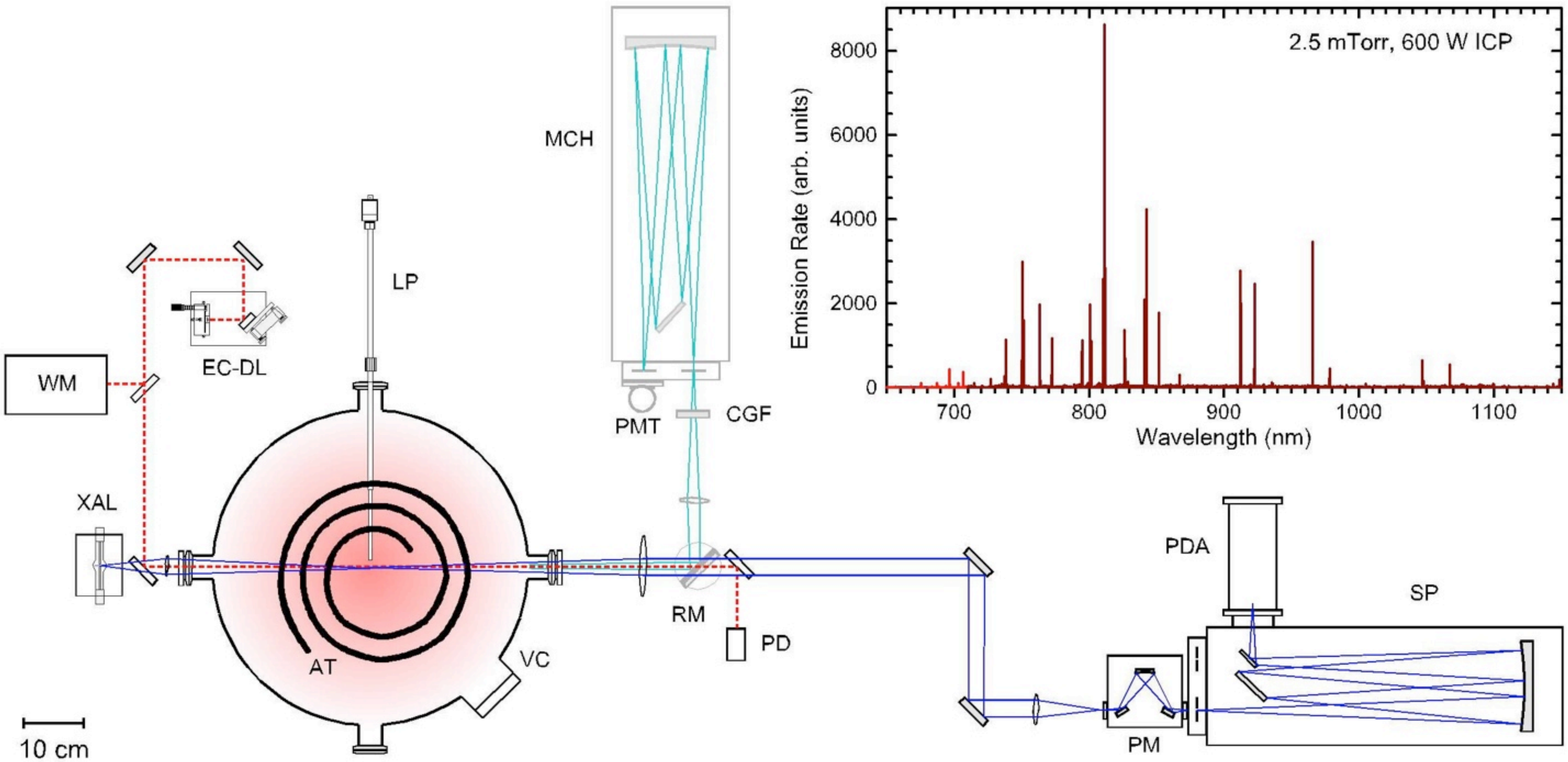
Argon emission spectrum

- Ultimate Goal: use emission spectra to extract encoded information about plasma conditions



Inductively coupled plasma (ICP)

- Operates in Ar and Ar mixtures at 13.56 MHz
- Electron energy distribution functions (EEDF)
  - Langmuir probes
  - optical diagnostics



Determining plasma properties from spectrum: emission model

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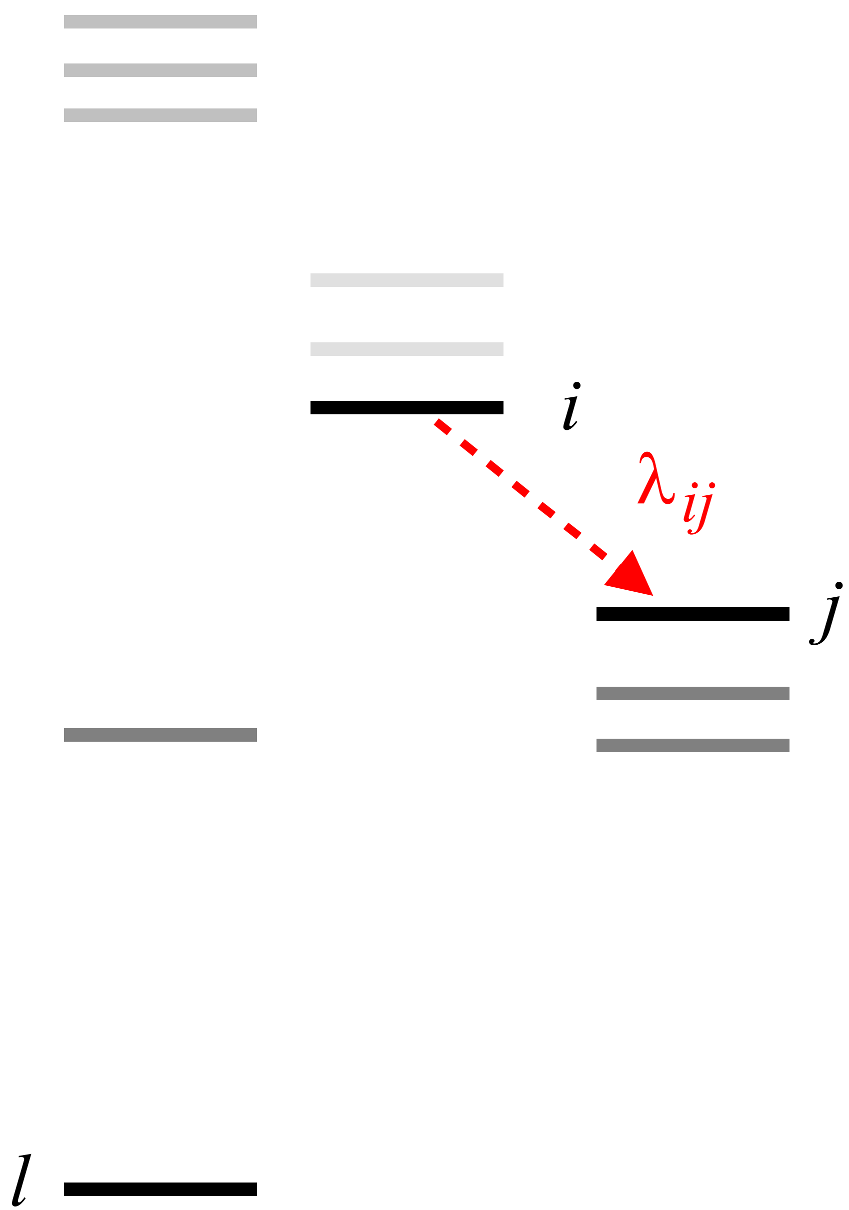
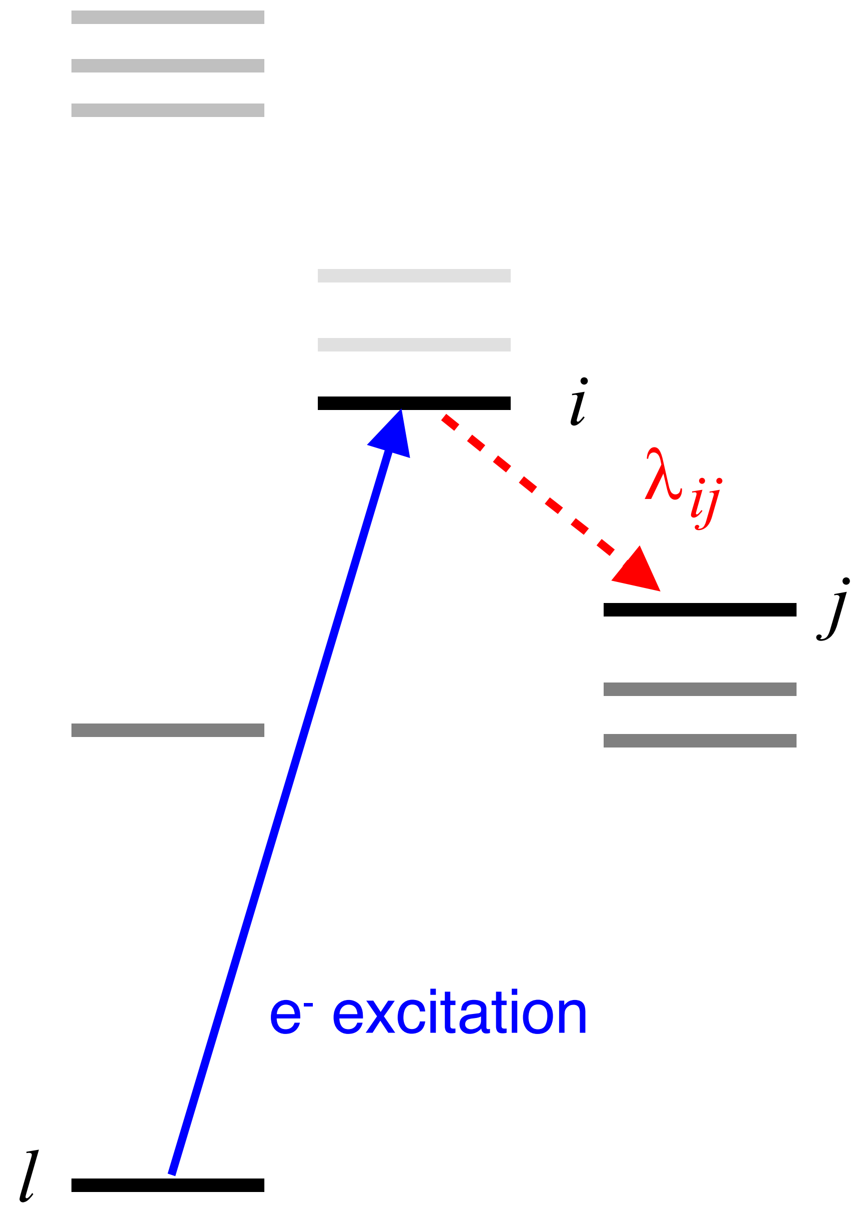
- Goal:
  - predict photon emission rate Φ_{ij} for $i \longrightarrow j$
- Approach:
  - account for mechanisms that populate emitting state - level *i*



Emission model

- Goal:
  - predict photon emission rate Φ_{ij} for $i \rightarrow j$
- Include:
  - electron excitation from level *l*
    - excitation probability is a function of electron energy
    - measured "cross sections" used to characterize excitation probabilities



Emission model - excitation cross sections

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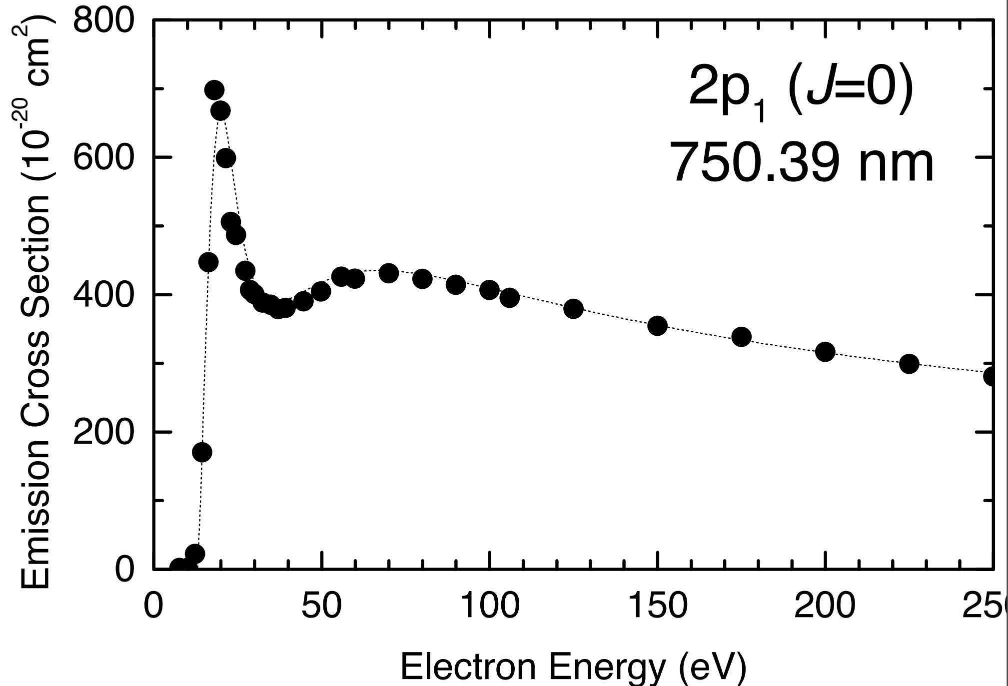
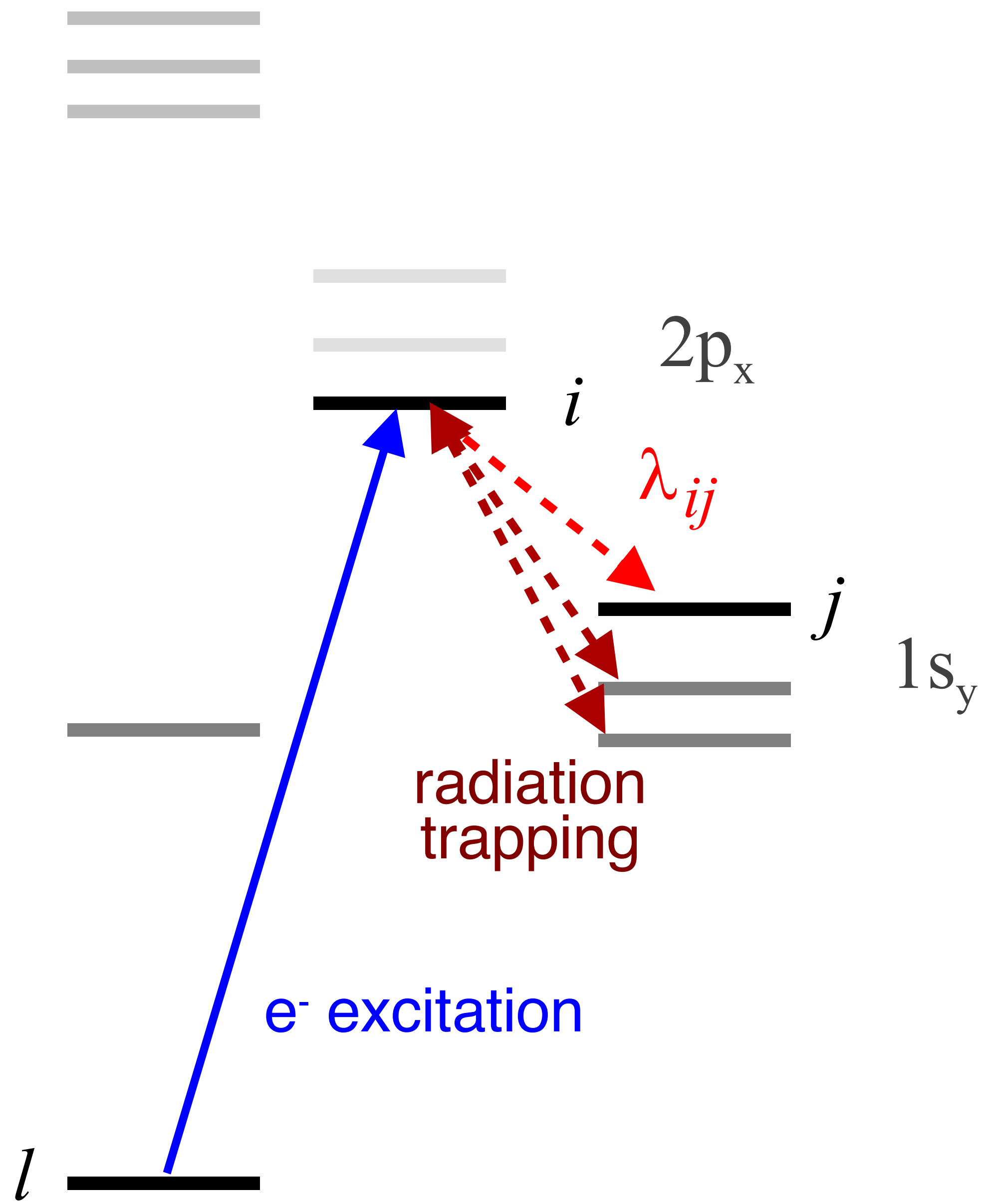
- cross section vs. electron energy
  - measure of electron impact excitation probability
  - key link between emission intensity and EEDF
  - measured by Prof. Chun Lin's group:
    - excitation from ground state
      - *Phys. Rev. A* **57**, 267 (1998)
      - *Phys. Rev. A* **68**, 032719 (2003)
      - *Ar. Data Nucl. Data Tables* **93**, 831 (2007)
    - excitation from metastable levels
      - *Phys. Rev. Lett.* **81**, 309 (1998)
      - *Phys. Rev. A* **59**, 2749 (1999)
      - *Phys. Rev. A* **75**, 052707 (2007)



Emission model - reabsorption

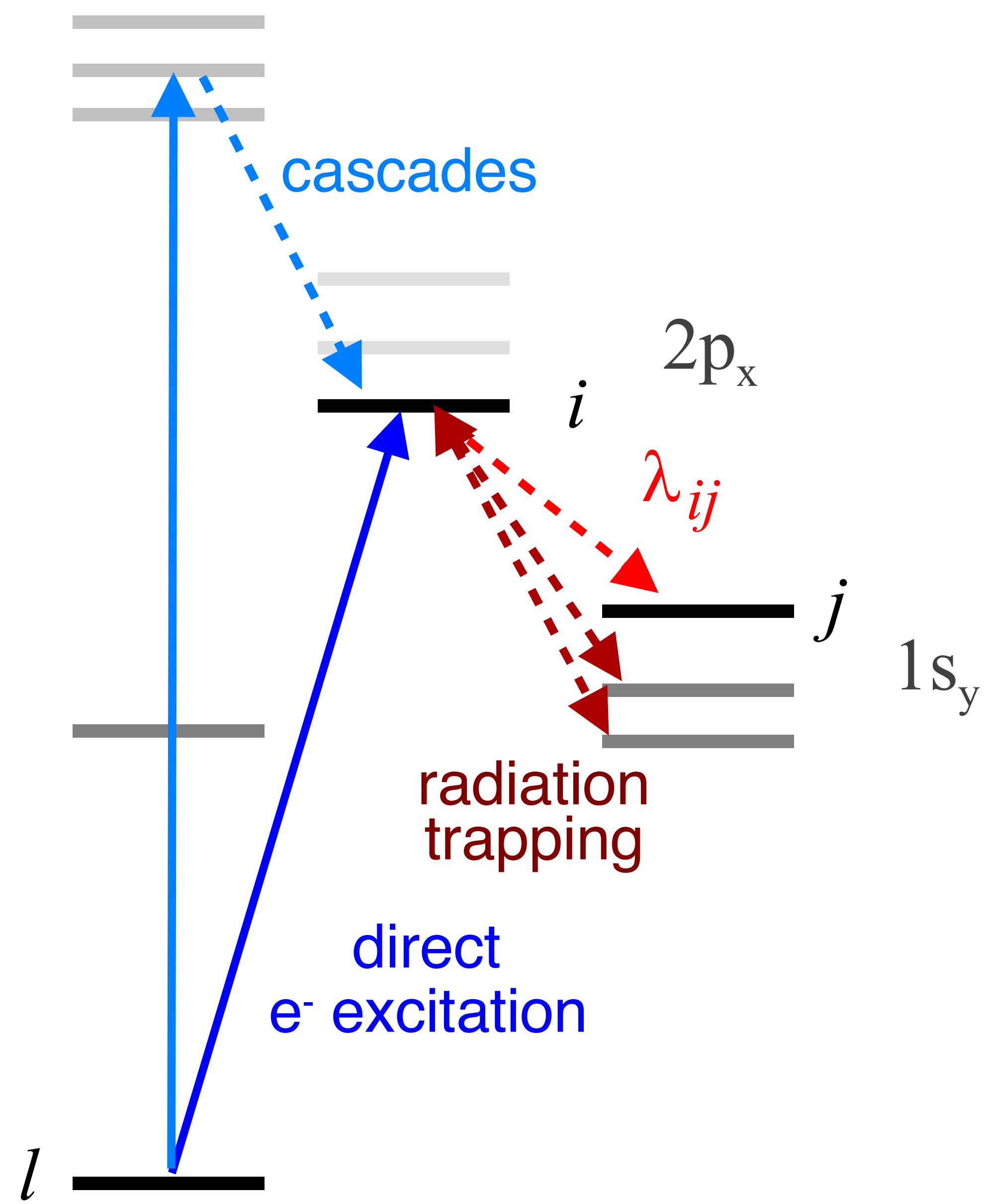
- Goal:
  - predict photon emission rate Φ_{ij} for $i \rightarrow j$

- Include mechanisms for populating level *i* :
  - electron excitation from level *l*
  - radiation trapping: excitation of metastables by photon absorption



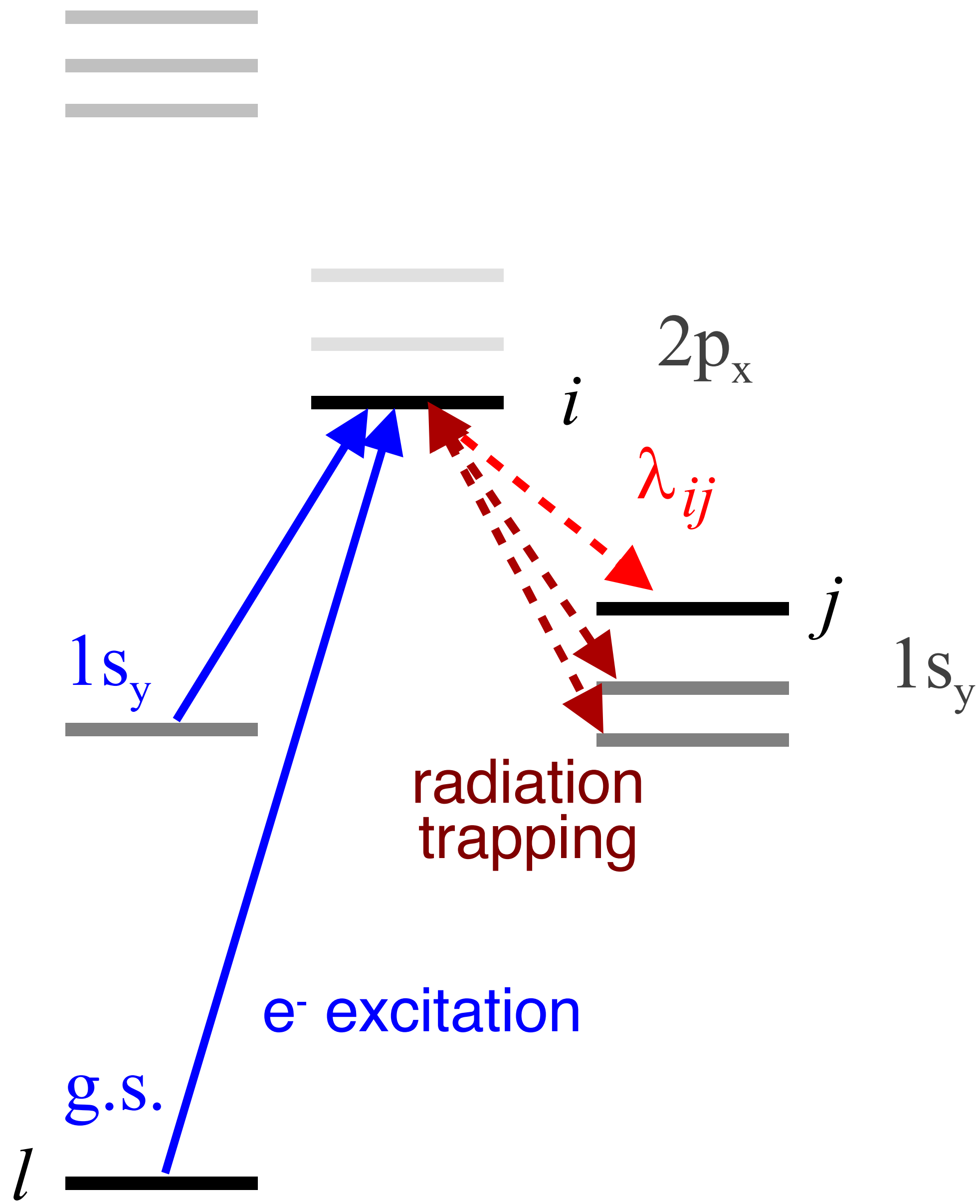
Emission model - cascades

- Goal:
  - predict photon emission rate Φ_{ij} for $i \rightarrow j$
- Include mechanisms for populating level *i* :
  - indirect electron excitation from level *l*
  - cascades from higher lying states
  - measured cross sections include cascades



Emission model - electron excitation of metastables

- Goal:
  - predict photon emission rate Φ_{ij} for $i \longrightarrow j$
- Include mechanisms for populating level *i* :
  - electron excitation:
    - from ground state
    - from metastable/resonance levels
  - photon reabsorption/trapping
    - from metastable/resonance levels



Excitation from resonance levels $1s_2$ & $1s_4$

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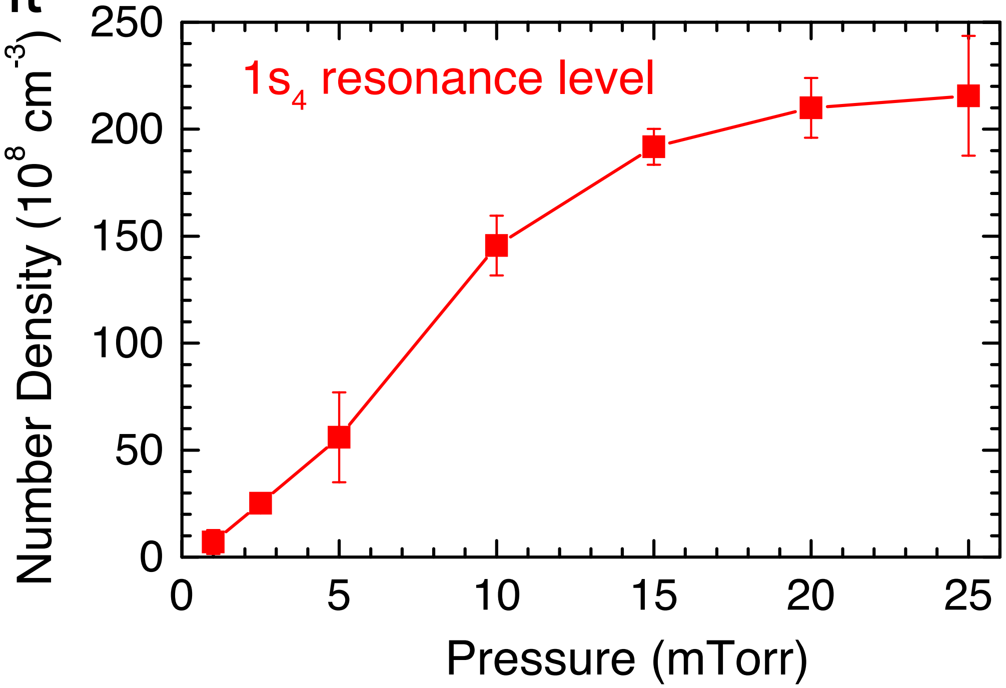
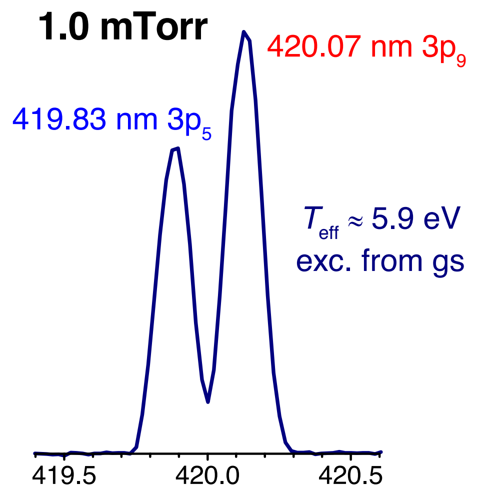
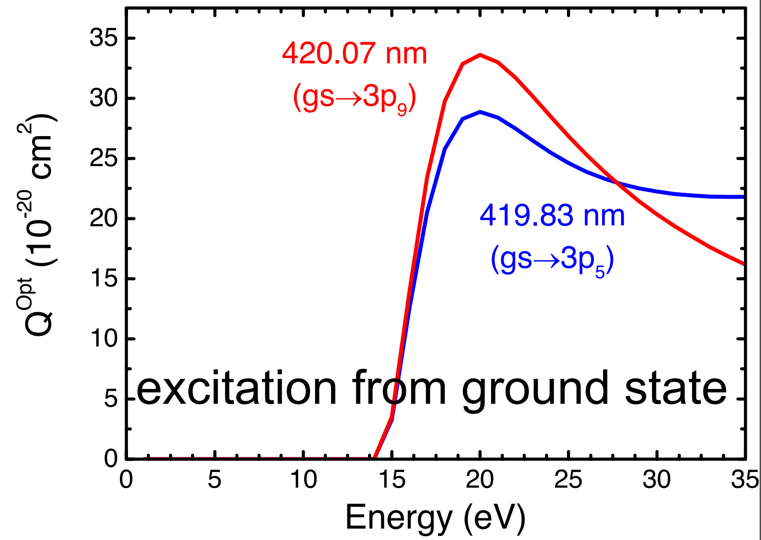
- $1s_3$ and $1s_5$ are *metastables*:
  - no radiative losses
  - high concentrations possible
- $1s_2$ and $1s_4$ populations significant when radiation is trapped:
  - $1s_2$ and $1s_4$ resonance levels:
    - have radiative decay channel to ground state
    - generally lower concentrations
    - exception: reabsorption when ground state density is high
  - *Electron impact excitation from resonance levels significant*
    - cross sections not measured
    - estimates used
    - *Adv. At. Mol. Opt. Phys.* **54**, 319 (2006)

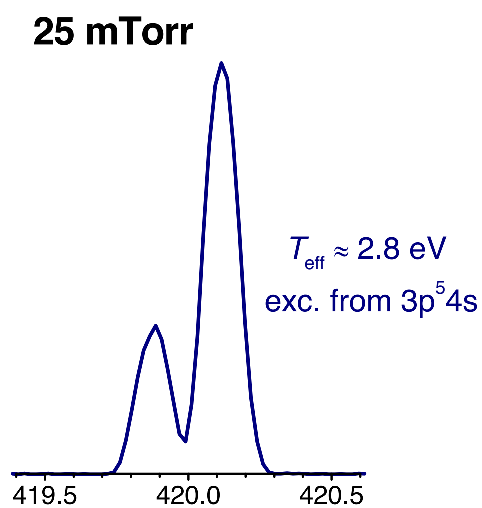


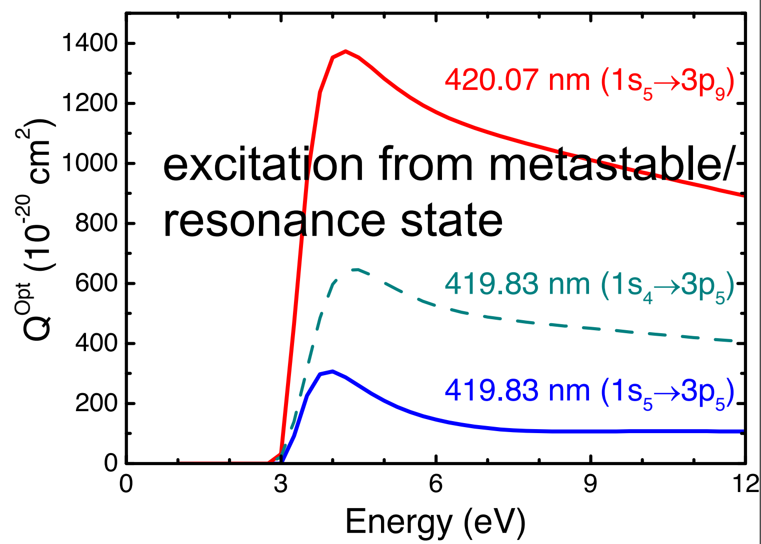
Cross sections: variations in threshold and energy dependence used in model

- 419.8 and 420.1 nm - close in wavelength
- difference between ground state and metastable cross sections
- large difference in peak intensities at 1 mTorr vs. 25 mTorr
  - higher ground state contribution at higher T_e





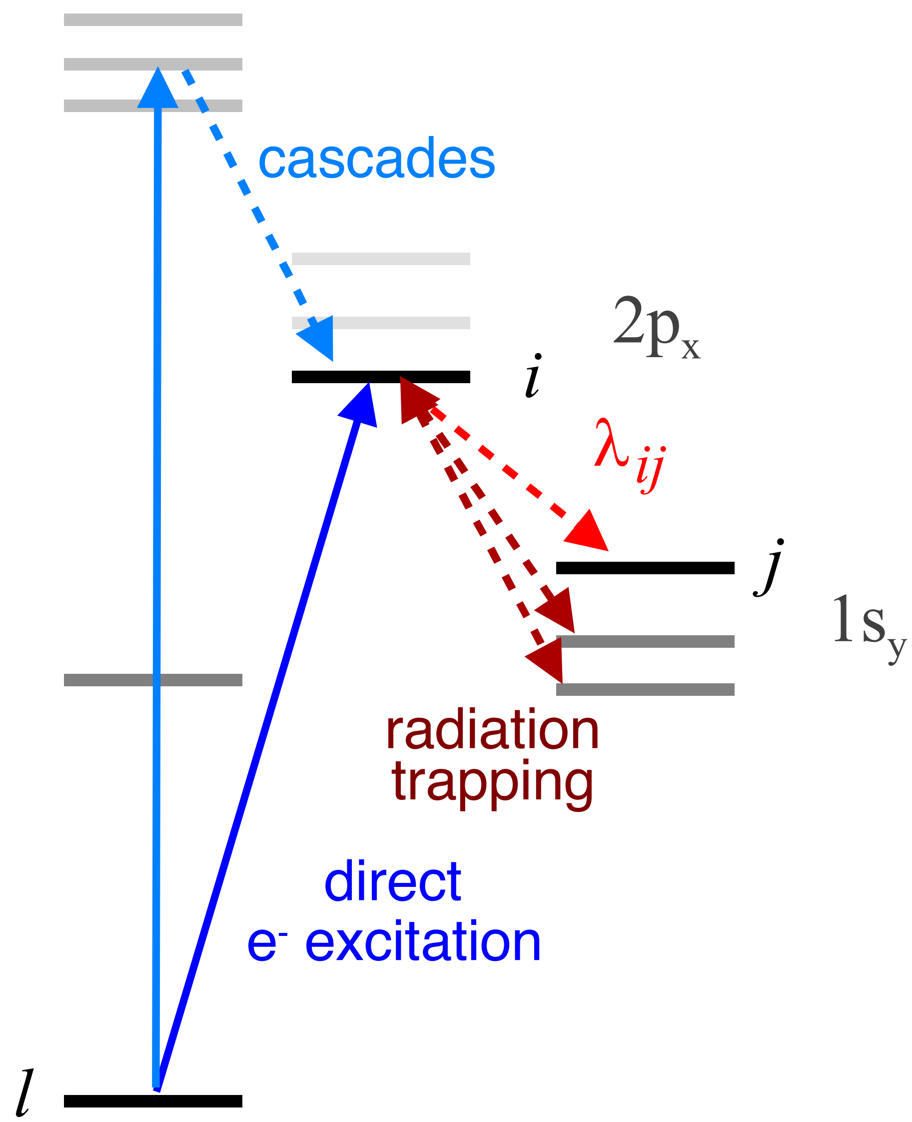




J. Phys. D. **45**:045201 (2012)

Emission model: summary

- Model goal:
  - predict photon emission rate Φ_{ij} for $i \longrightarrow j$
- Effects included:
  - electron excitation from level *l*
    - cascades
    - metastable contribution
  - radiation trapping
- Needed inputs
  - atomic data (A_{ij}, cross sections,...)
  - electron energy distribution function
  - number densities (ground state AND $1s_y$ for argon)



Emission model: intensity of $i \to j$ transition

$$\Phi_{ij} = K n_e R_{ij} \left[\sum_l n_l k_{ij}^l \right]$$

- sum over initial level *l* (ground state, $1s_2$, $1s_3$, $1s_4$, $1s_5$)
- k^l_{ij} is the electron impact excitation rate
  - depends on cross sections, EEDF

$$k_{ij}^l = \sqrt{\frac{2}{m_e}} \int_0^\infty Q_{ij}^l(E) f_e(E) \sqrt{E} dE$$

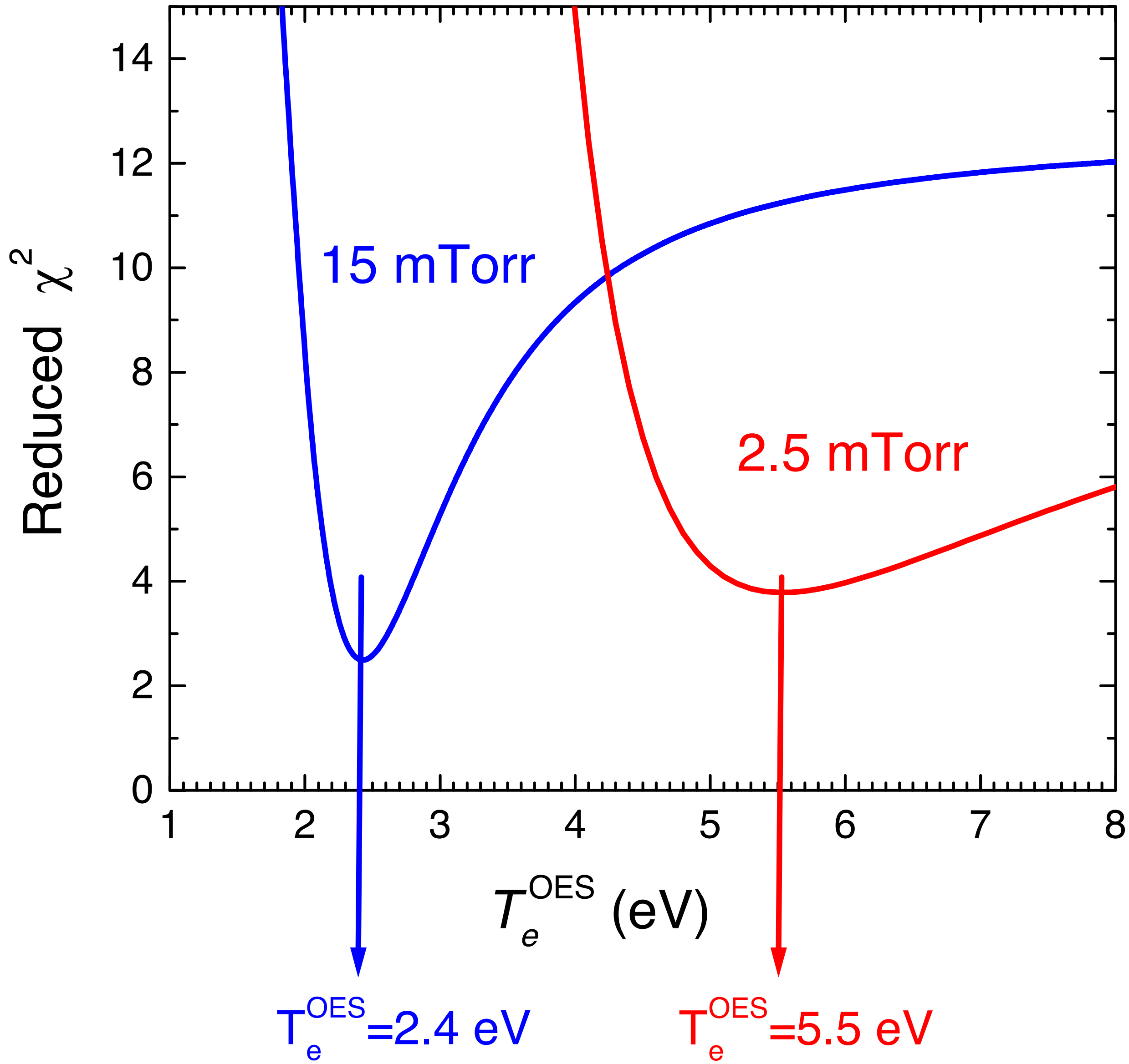
- reabsorption correction factor R_{ij} is function of $1s_y$ concentrations
- use ratios to standard line to eliminate K, n_e

$$\frac{\Phi_{ij}}{\Phi_{i'j'}} = \frac{R_{ij} \sum_l n_l k_{ij}^l}{R_{i'j'} \sum_l n_l k_{i'j'}^l}$$

- calculate line ratios for multiple trial EEDFs
- seek EEDF giving best match to observed line ratios

Trials for Maxwellian EEDF

- minimum χ^2 gives best fit electron temperature



Emission model predictions

- contributions from ground state vs. $1s_y$ levels

2.5 mTorr

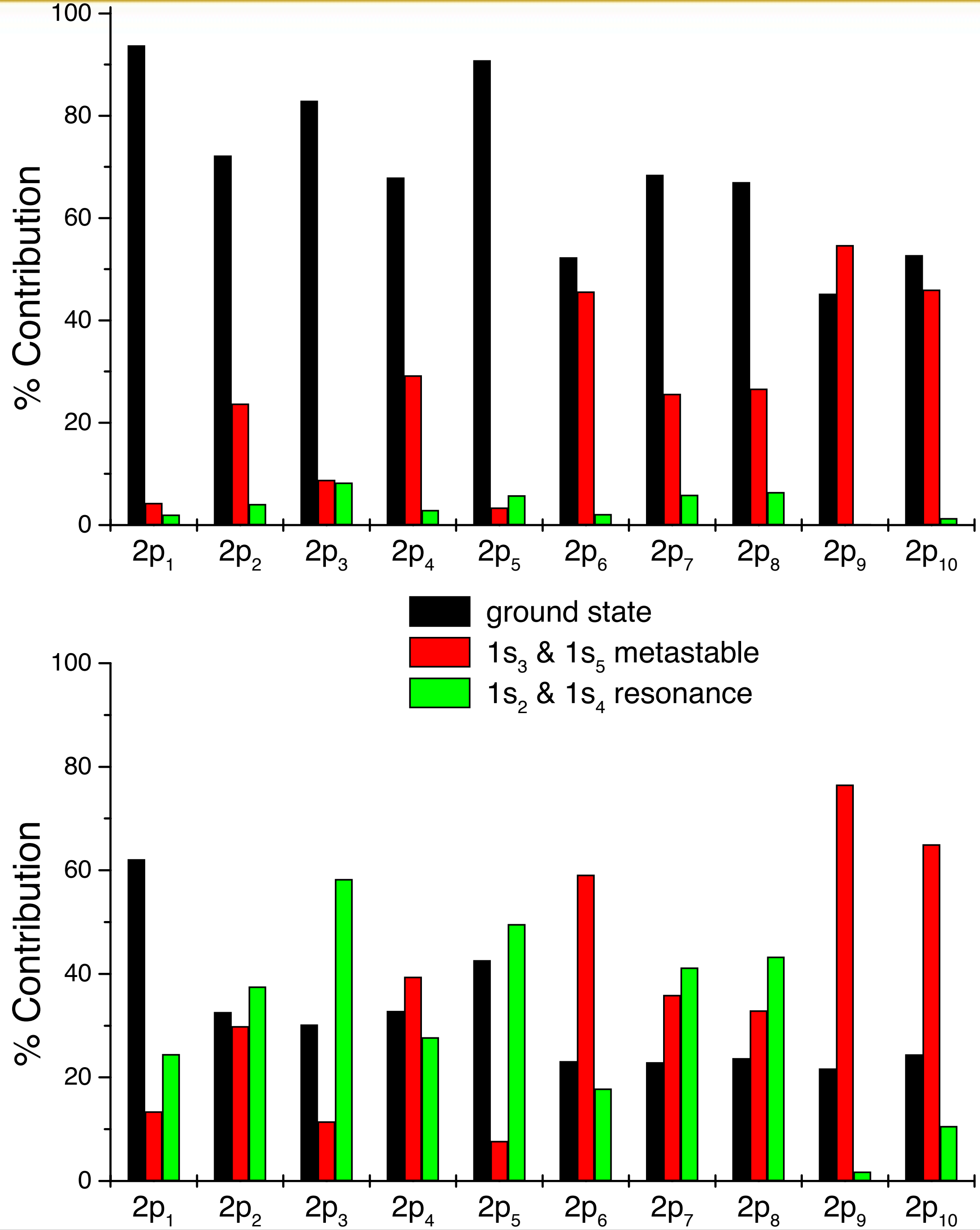
T_{eff} = 5.4 eV

$n_m/n_0 = 1.4 \times 10^{-3}$

15 mTorr

T_{eff} =2.7 eV

$n_m/n_0 = 3.2 \times 10^{-4}$

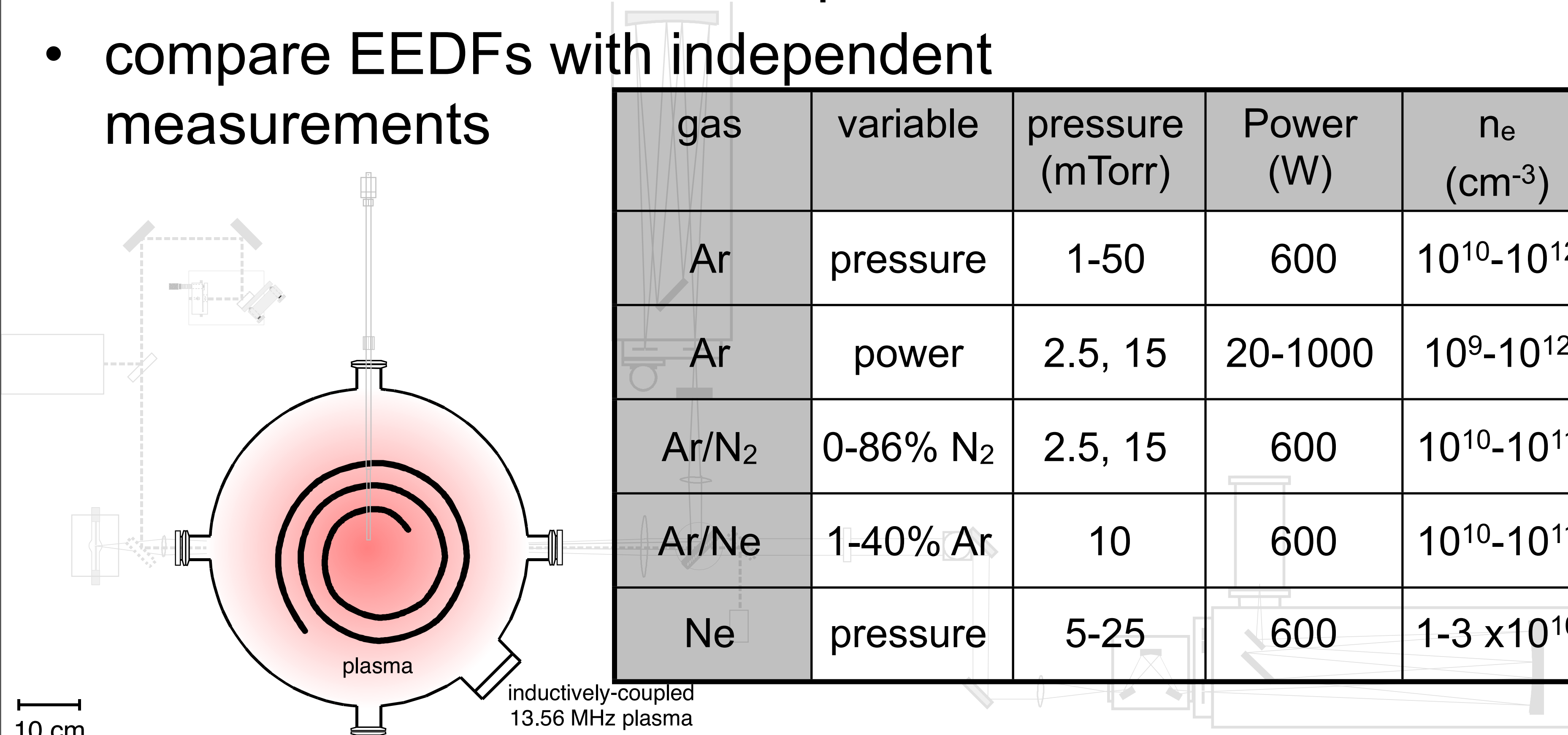


Application:
Non-maxwellian EEDFs in ICPs

Inductively coupled plasma source

- 2.5 turn flat coil antenna
- 13.56 MHz
- 50 cm diameter chamber
- measure emission model inputs
- compare EEDFs with independent measurements

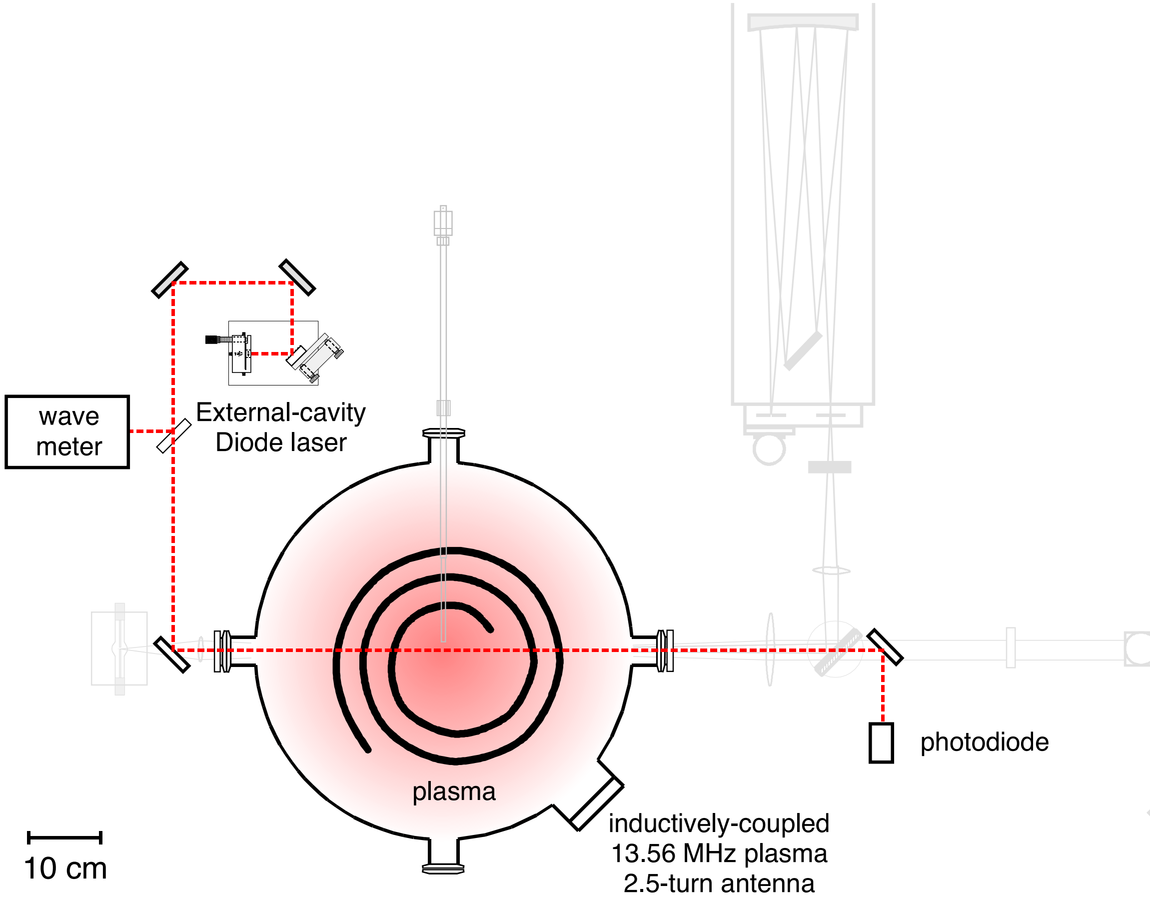
gas	variable	pressure (mTorr)	Power (W)	n_e (cm^{-3})	T_e (eV)
Ar	pressure	1-50	600	10^{10}-10^{12}	2-6
Ar	power	2.5, 15	20-1000	10^{9}-10^{12}	5, 3
Ar/N_2	0-86% N_2	2.5, 15	600	10^{10}-10^{11}	5, 3
Ar/Ne	1-40% Ar	10	600	10^{10}-10^{11}	3-6
Ne	pressure	5-25	600	1-3 x10^{10}	5-7

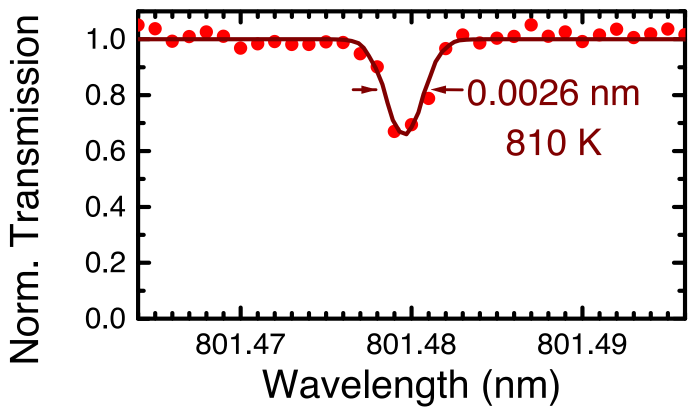


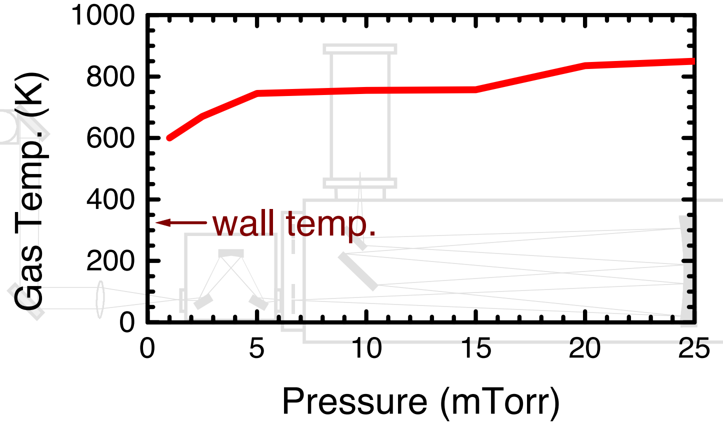
inductively-coupled 13.56 MHz plasma 2.5-turn antenna

Model input: ground state density

- $n_0 = p/kT_{gas}$
- gas temperature determined with laser absorption spectroscopy
- Doppler width of $3p^54s$-$3p^54p$ transition line

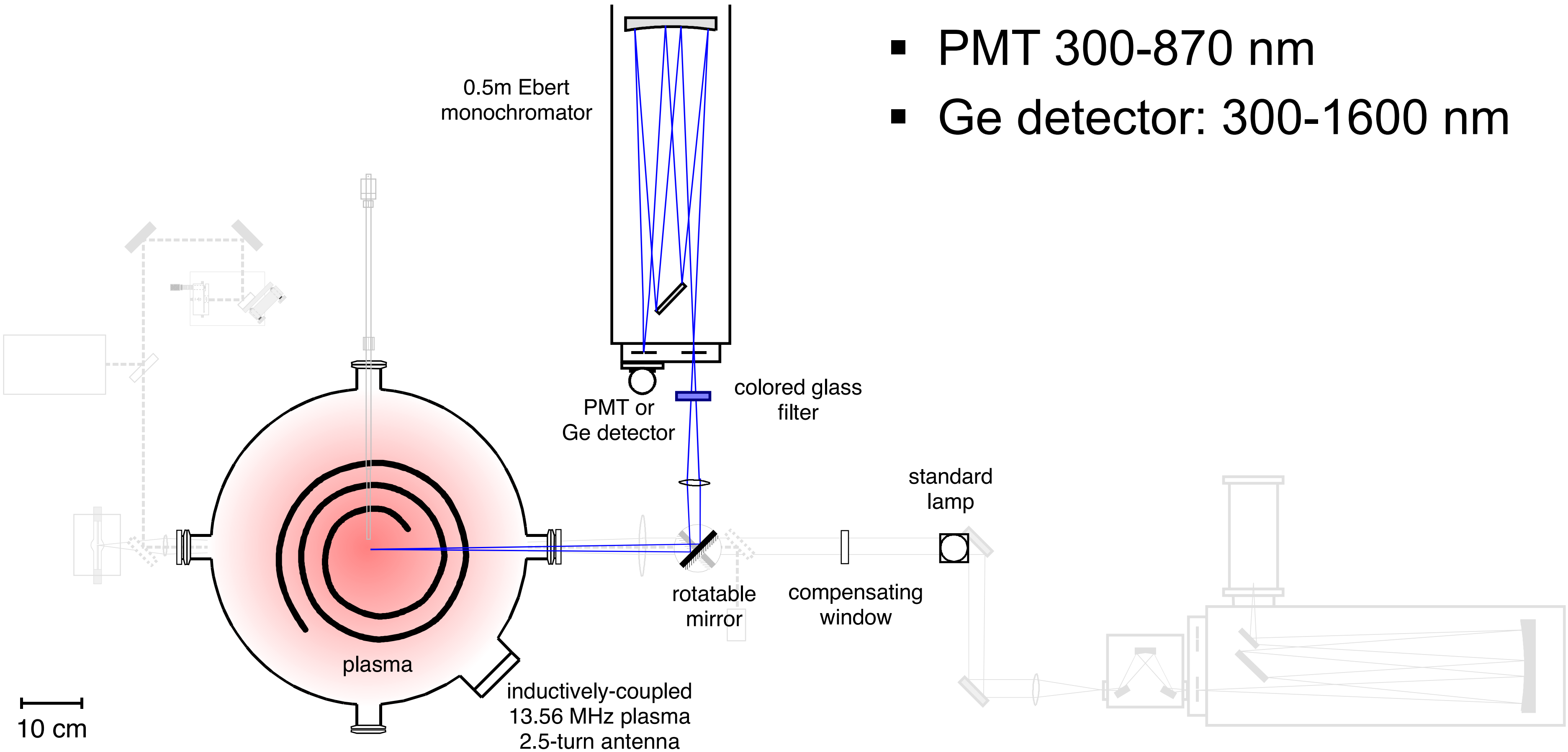






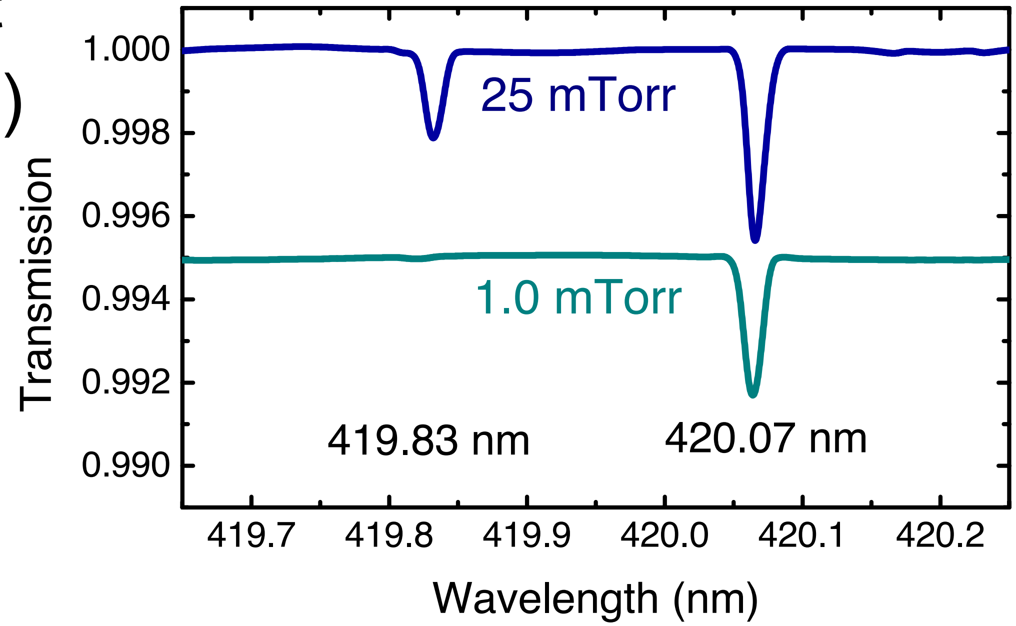
Model input: optical emission spectrum (OES)

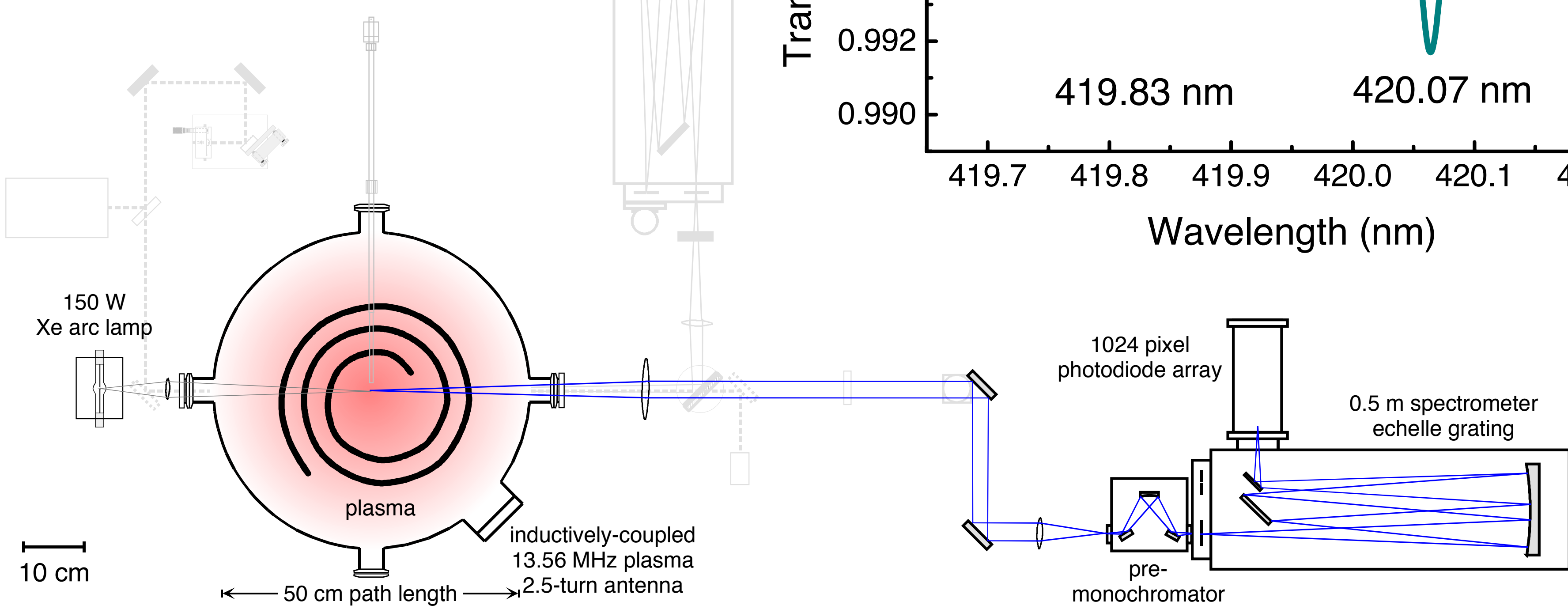
- 300-1600 nm wavelength range
- 0.13 nm resolution
- Detectors:
  - PMT 300-870 nm
  - Ge detector: 300-1600 nm



Model input: $1s_y$ concentrations

- Method #1: optical absorption spectroscopy (OAS)
  - white light absorption
  - column density measurement
- Method #2: OES (next slide)





Metastable/resonant densities from OES

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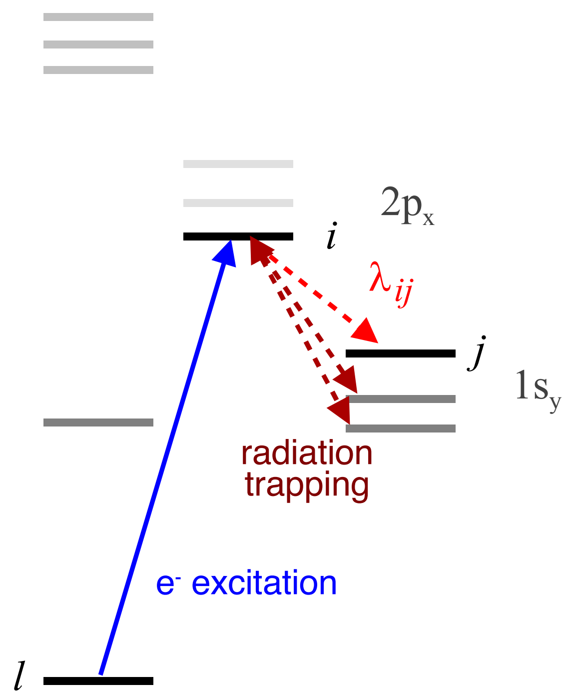
- Method #2: OES
- OES preferable due to simplified instrumentation
- OES branching fraction technique:
  - takes advantage of reabsorption by $1s_y$ metastable and resonance levels
  - reabsorption changes branching fractions
  - use ratio of lines from same *upper* state

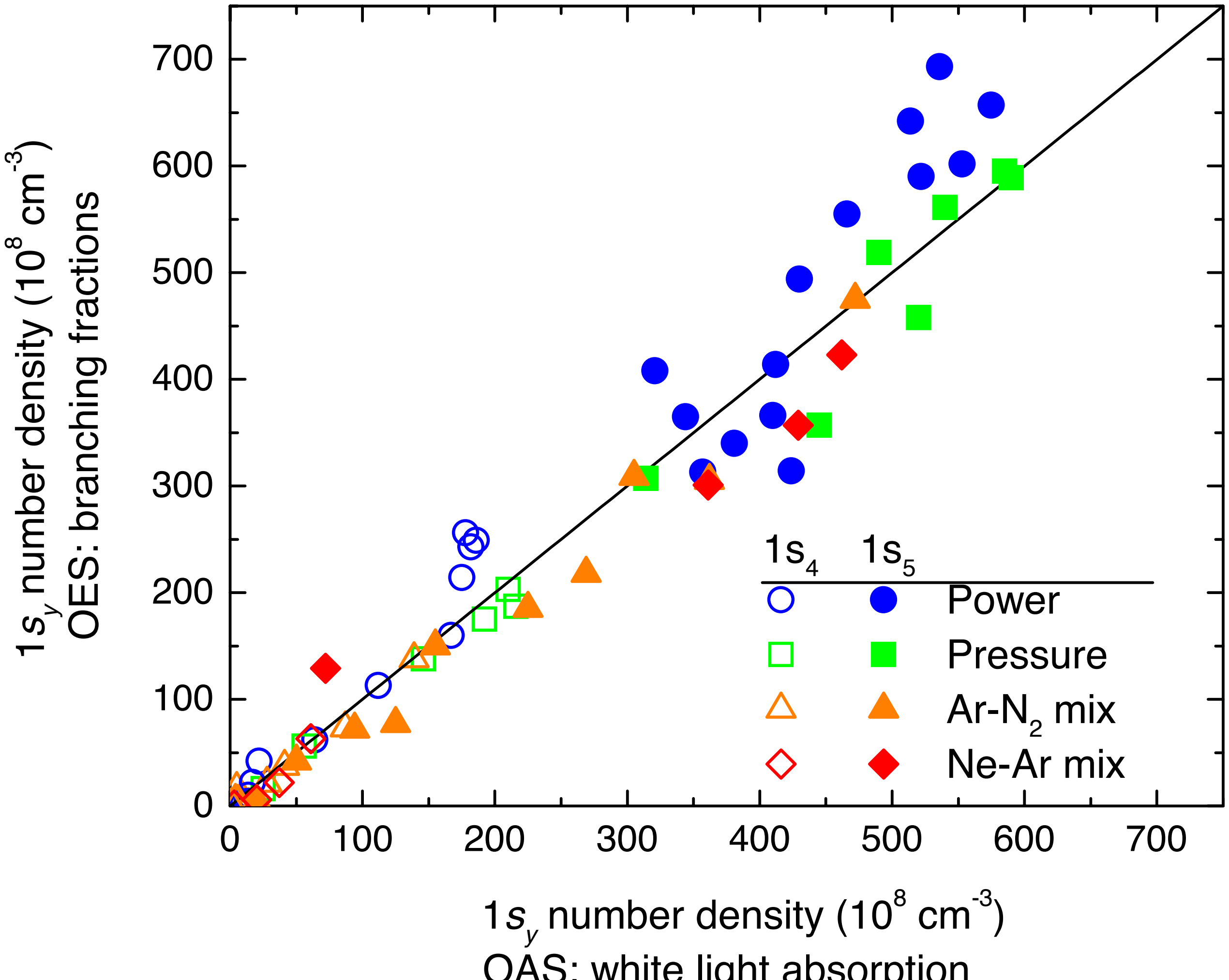
$$\frac{\Phi_{ij}}{\Phi_{ij'}} = \frac{A^0_{ij}}{A^0_{ij'}} \frac{g[\kappa_{ij}(n_j)\rho]}{g[\kappa_{ij'}(n_{j'})\rho]}$$

  - extract set of n_j densities from fit of model to observed ratios of different line pairs



Metastable/resonant densities from OES

- OES method agrees with OAS over wide parameter range
  - simple, non-invasive method to determine $1s_y$ densities

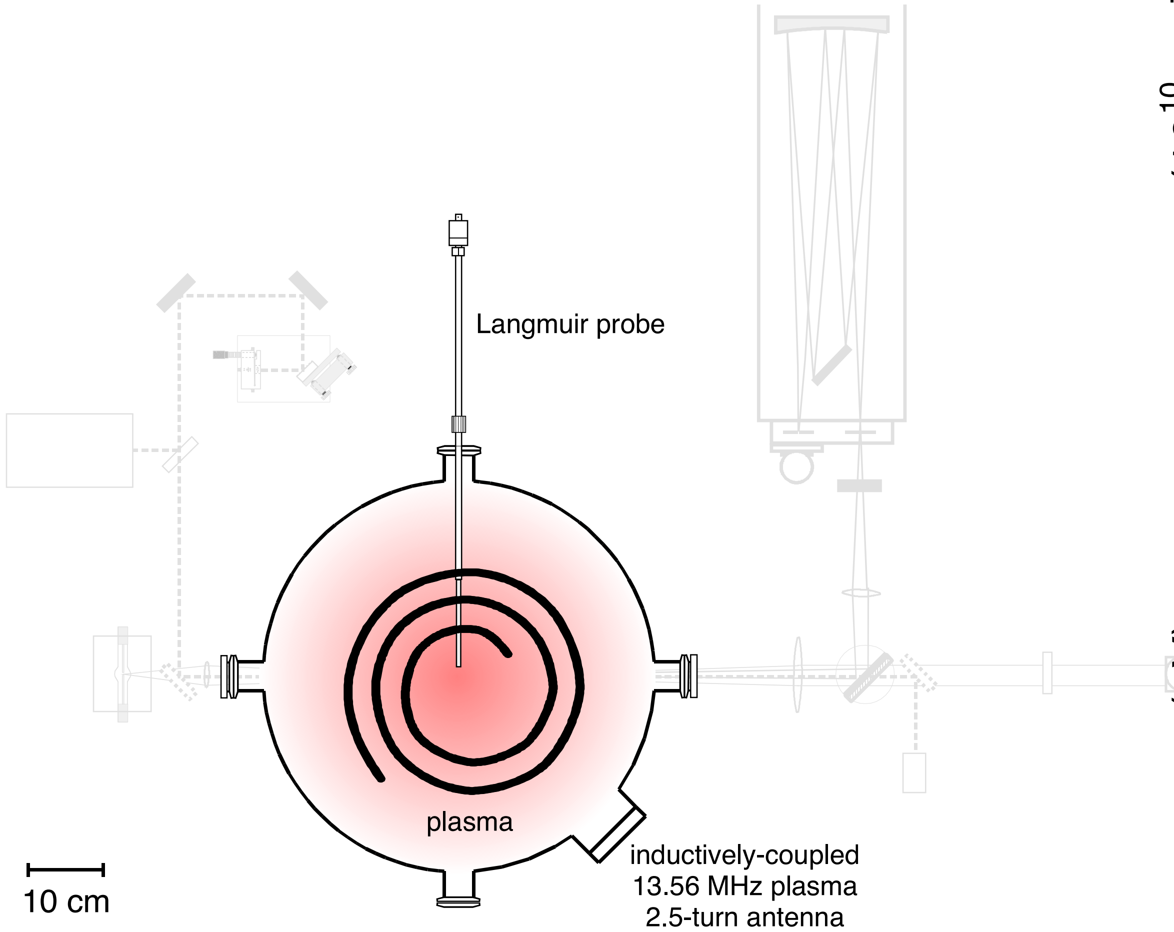


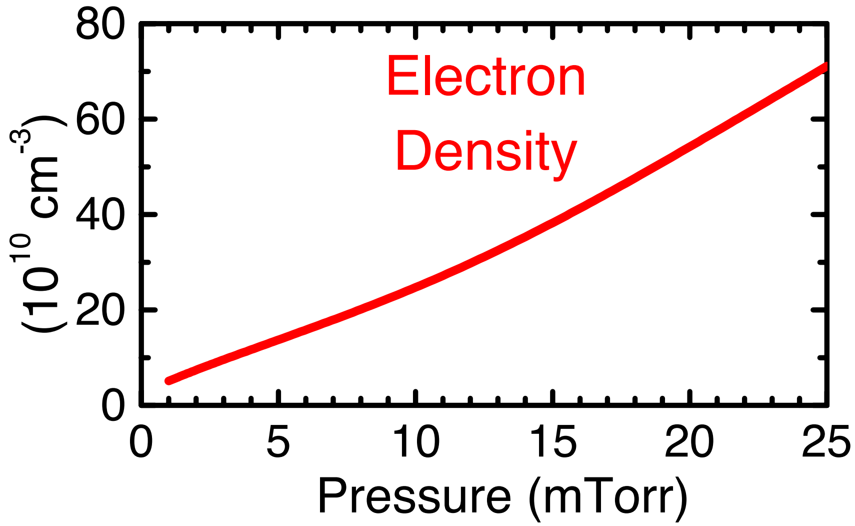
J. B. Boffard *et al.*, *PSST* **18**:035017 (2009).

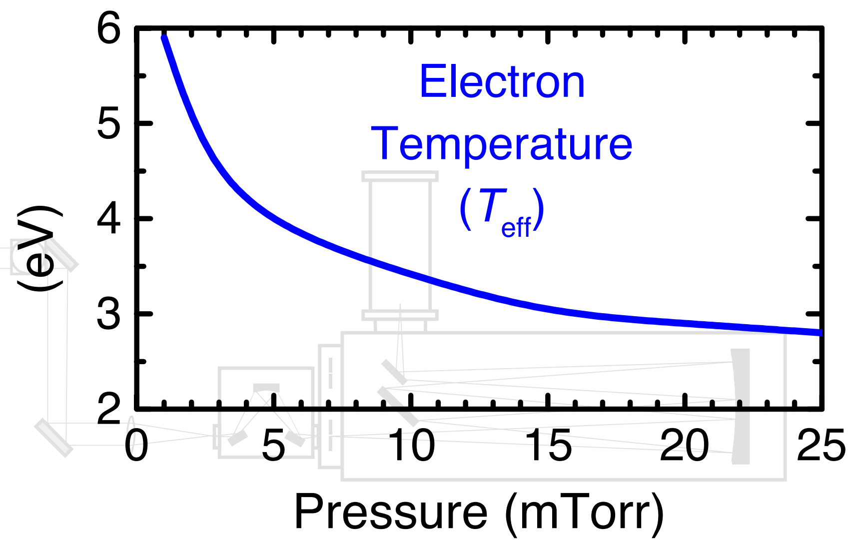
Compare emission model with EEDF from Langmuir probe

$$f_e(V) = \frac{2m_e}{e^2 A} \sqrt{\frac{2eV}{m_e}} \frac{d^2 I}{dV^2}$$

- compare to emission model output

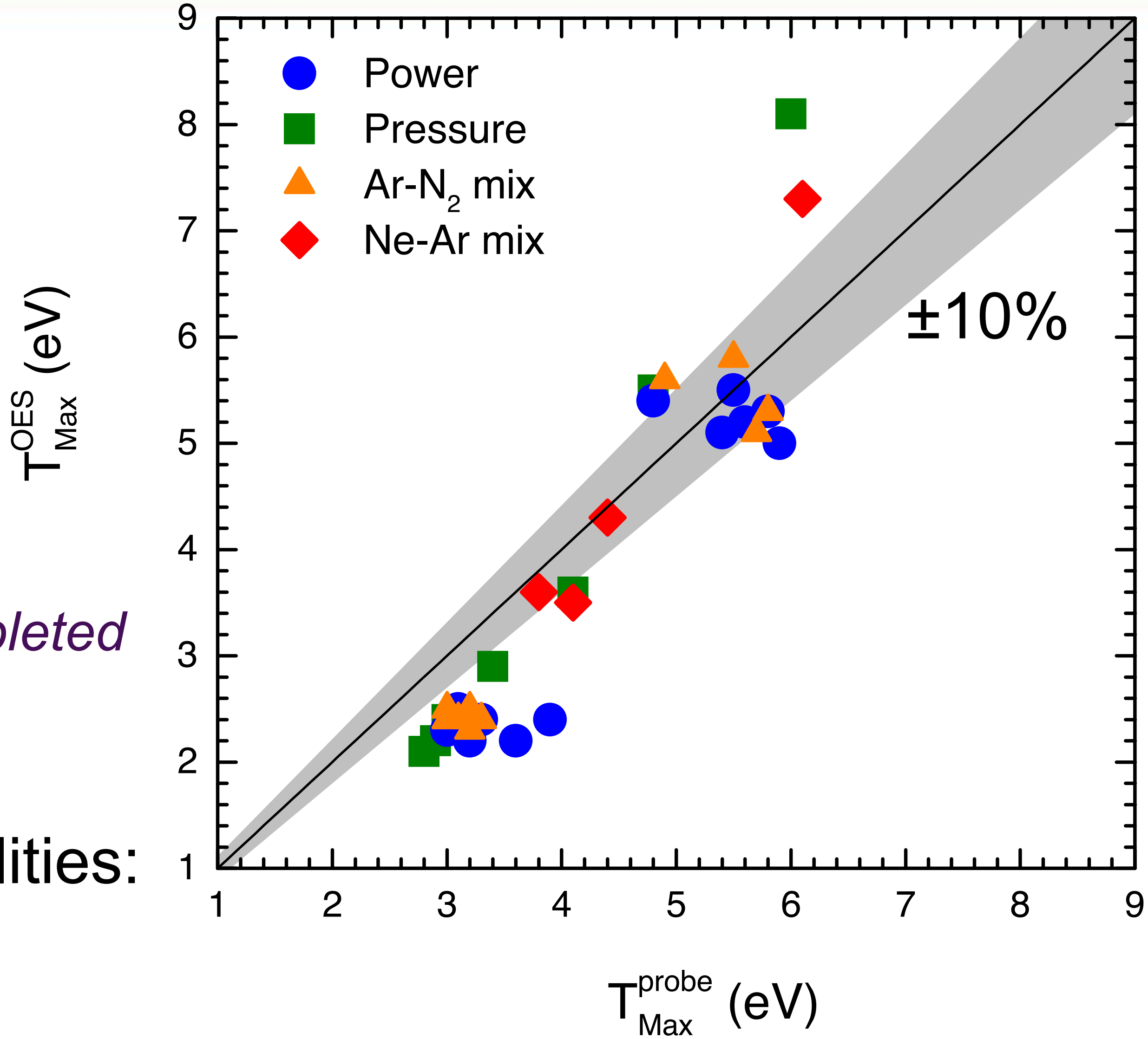






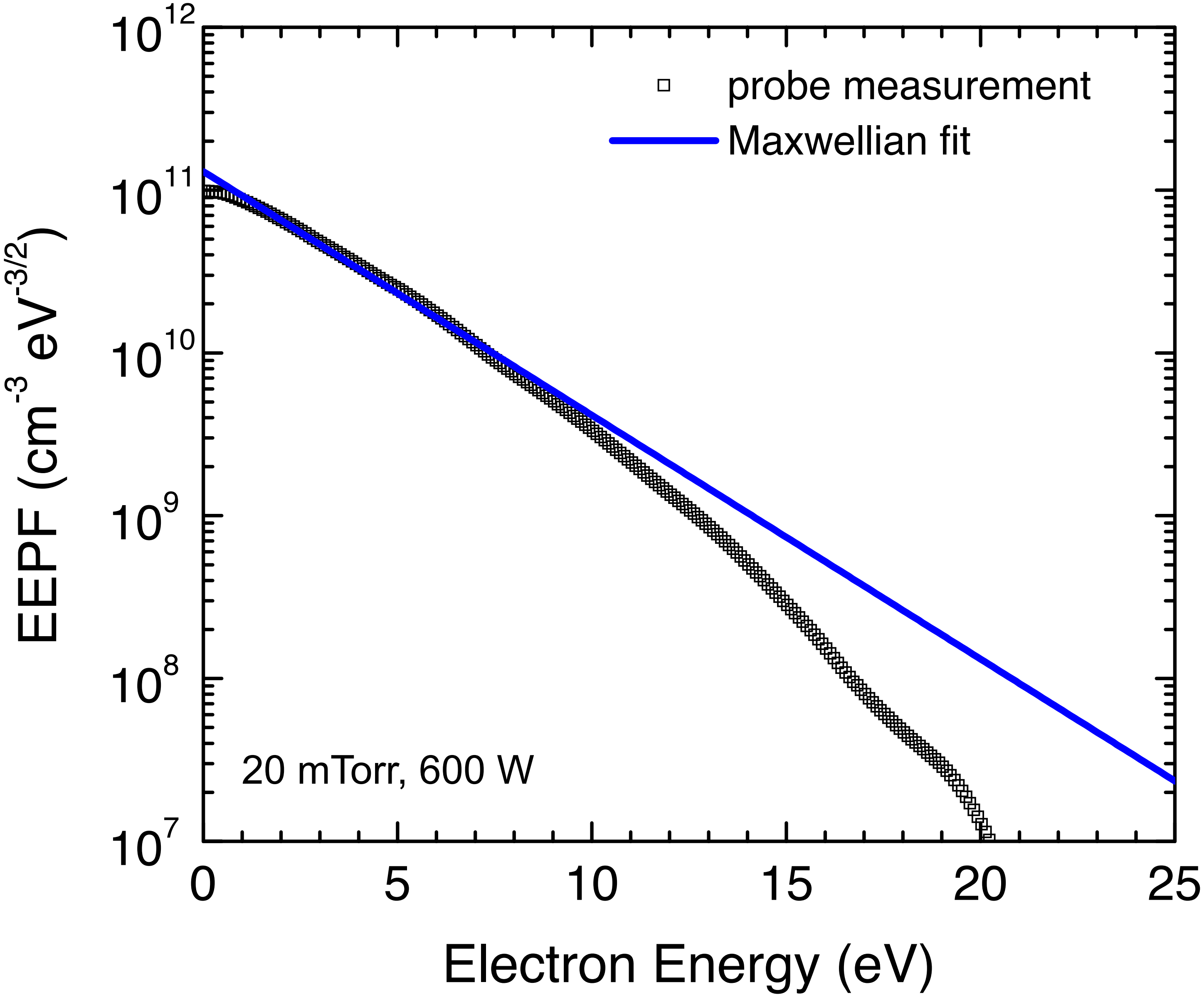
Comparison assuming *Maxwellian* EEDF

- T_e computed from
  - emission model
  - Langmuir probe fit
  - *agreement not great*
- reason for poor fit
  - EEDF is *not* Maxwellian
  - *actually, EEDF "tail" is depleted compared to Maxwellian*
- other (less likely) possibilities:
  - incorrect n_l values
  - incorrect cross sections



Non-Maxwellian EEDF

- Langmuir probe measurement in ICP shows "tail" depletion

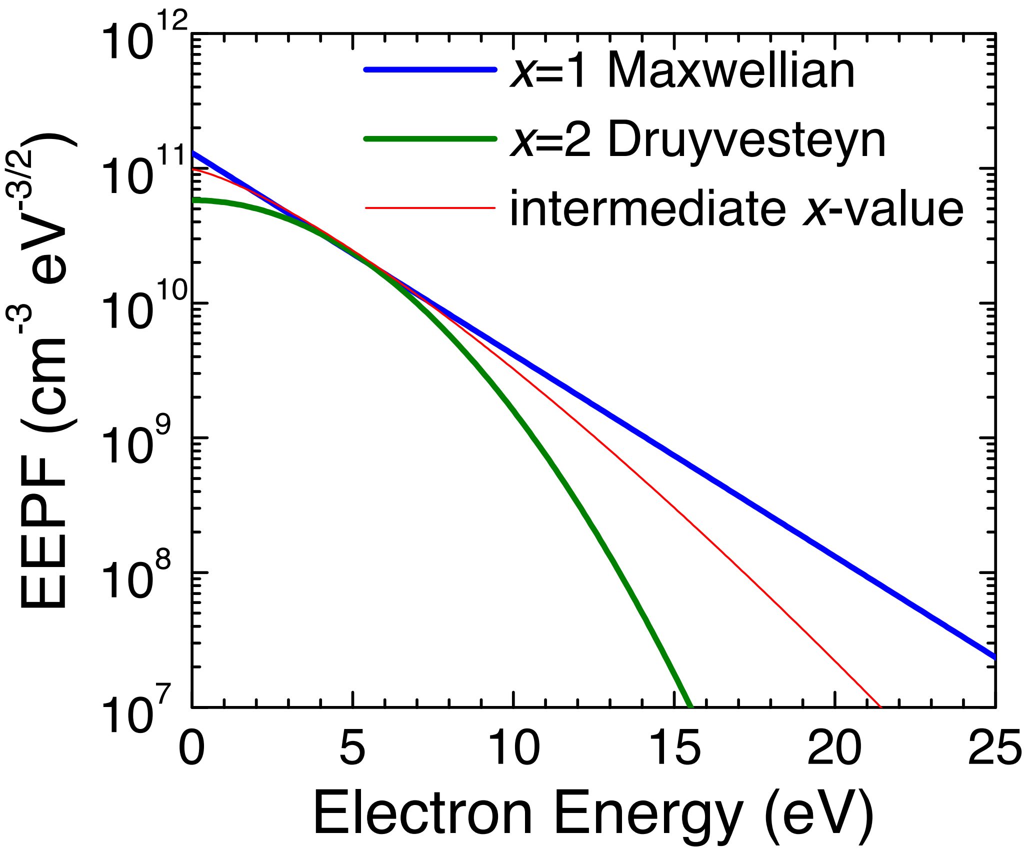


Representing EEDF in emission model

- Goal: account for non-Maxwellian energy dependence
- use "generalized *x*-form"

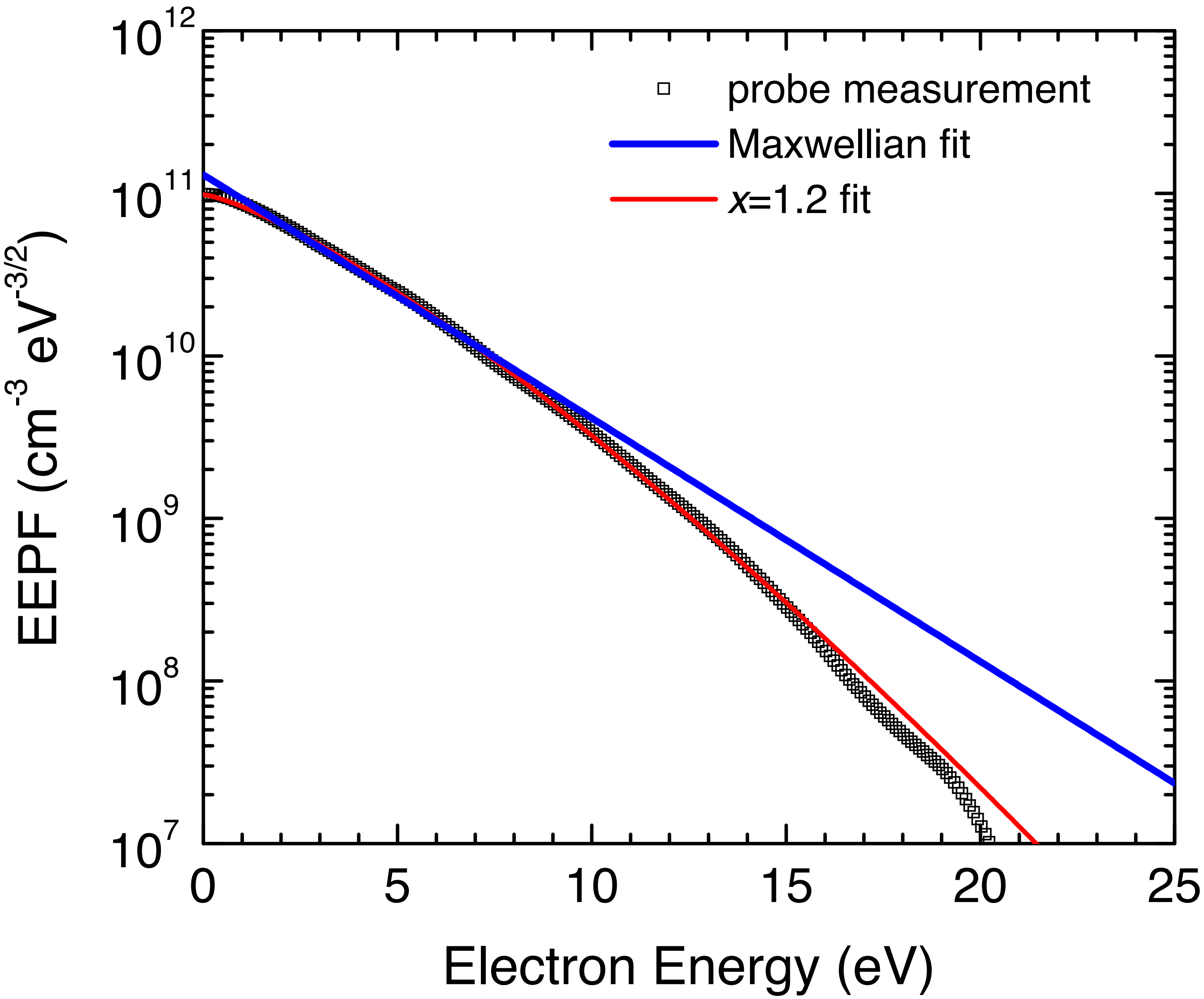
$$f_x(E) = c_1 T_x^{-3/2} \sqrt{E} e^{-c_2 (E/T_x)^x}$$

- T_x is an *effective* electron temperature (T_x=2/3<E>)
- c_1 and c_2 are functions of x
- x=1 corresponds to a Maxwellian
- x=2 corresponds to a Druyvesteyn
- x-form good fit for most ICP conditions



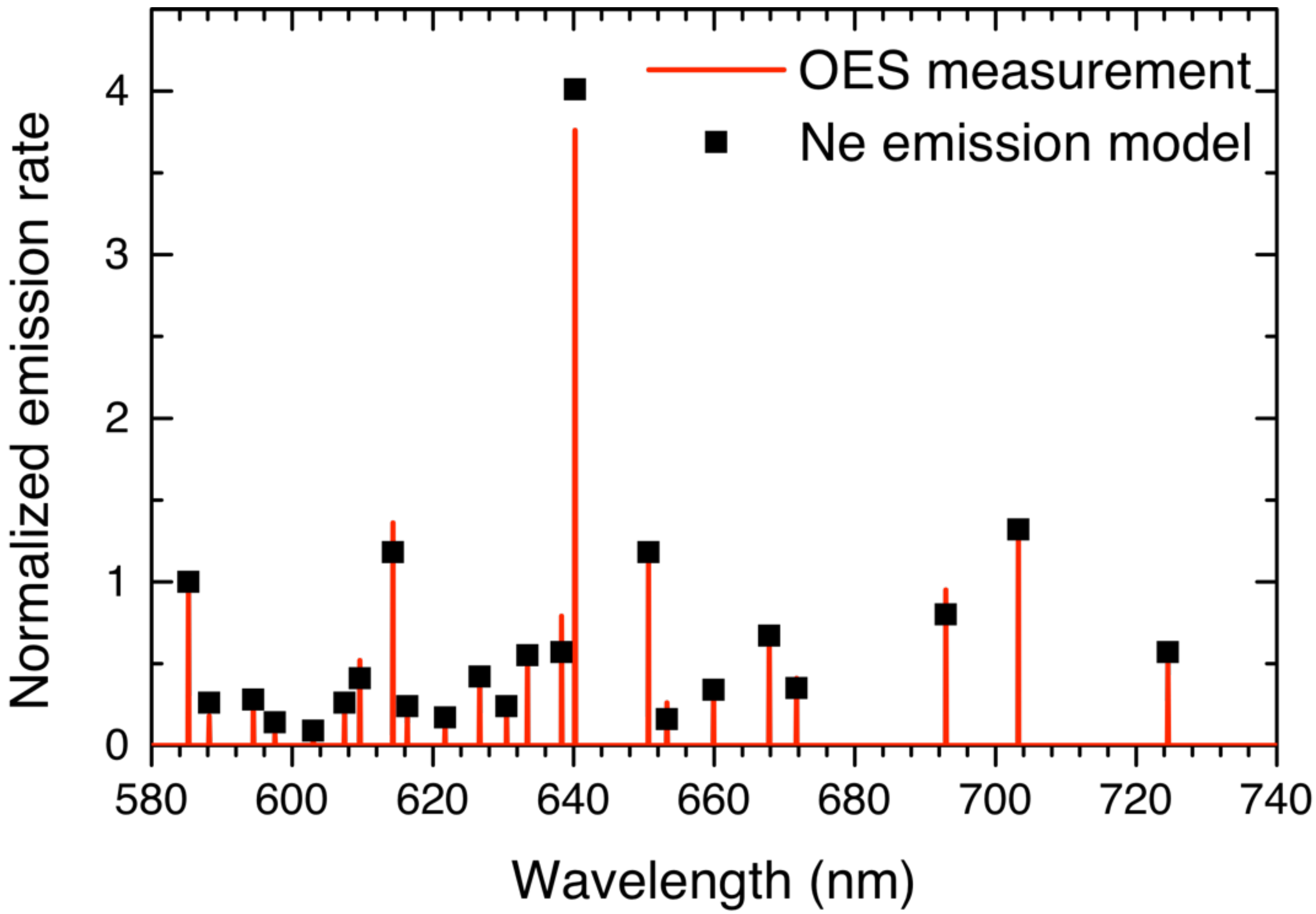
EEDF with x=1.2

- example shows improved fit to Ar probe data
- x ranges from x=1.2 to x=1.6 for Ar ICP



OES also produces x=1.2

- emission model agrees well with measurement*



*Plasma Sources Sci. Technol. 19 (2010) 065001.

Extension to Ar($3p^5 5p$) emissions - limitations

- $3p_x$ levels have longer radiative lifetimes than $2p_x$ levels
  - $2p_x$ levels: 20-35 ns
  - $3p_x$ levels: 80-160 ns

- Longer radiative lifetime increases chances of electron-atom collision while atom is in excited level
  - electron-quenching: non-radiative decay out of level
  - electron-transfer: excitation from $3p_x$ to another $3p_x$' level
  - emissions redistributed
  - need modified emission model

- *Bonus*: modified emission model predicts electron density

Emission model including 2p and 3p

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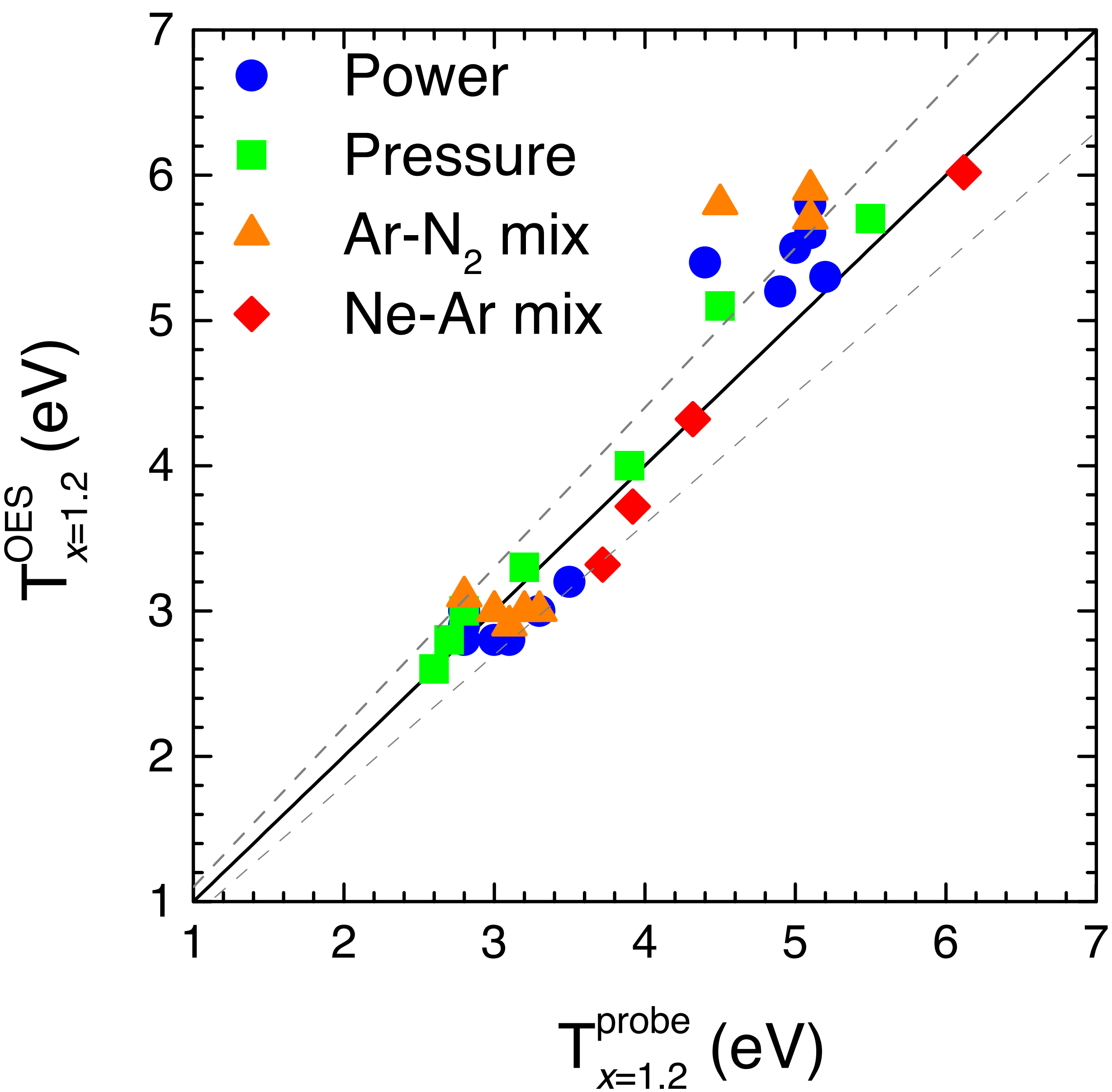
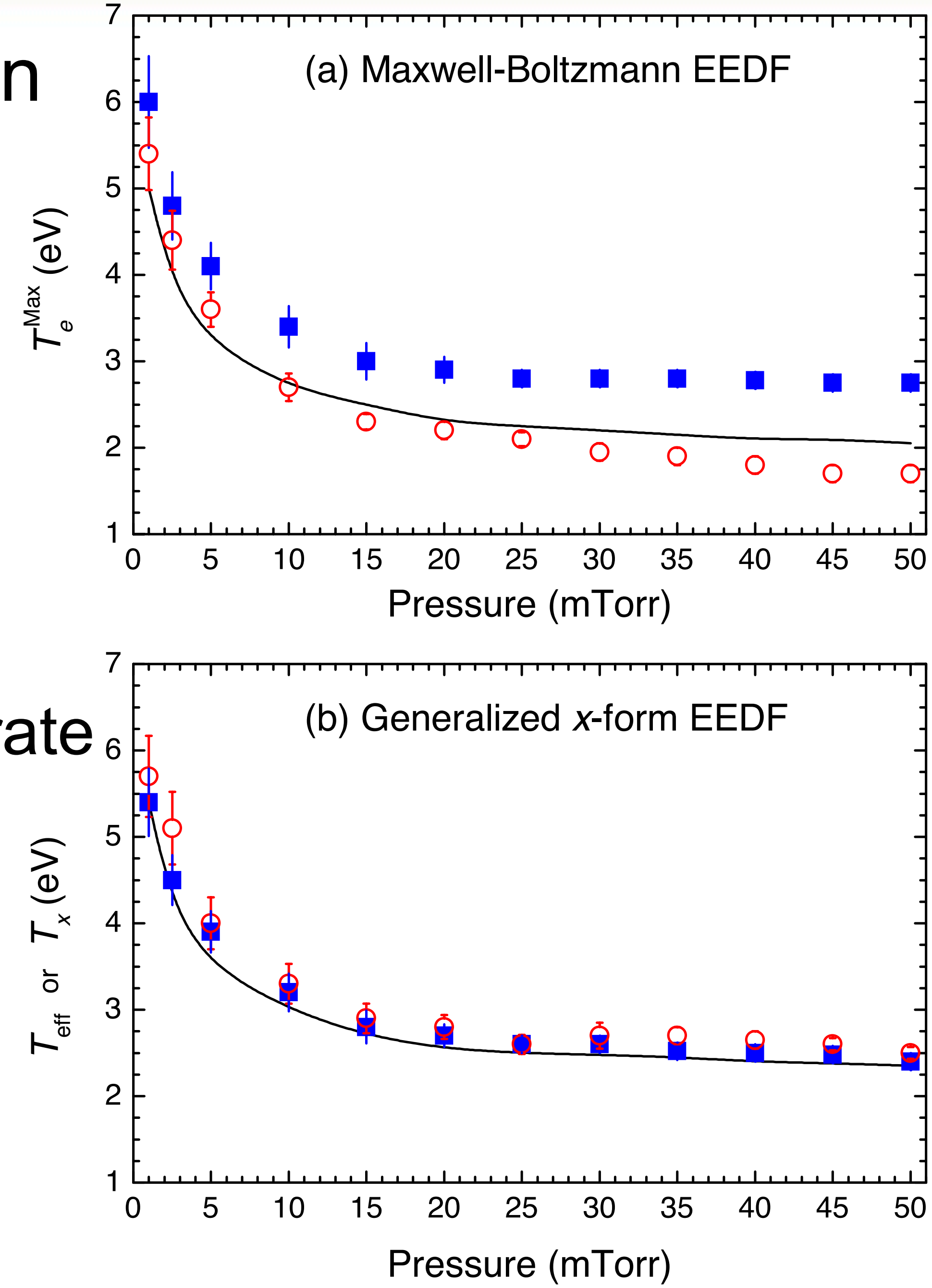
- agreement with probe: ±7%



Ar pressure dependence

- Comparison of a) Maxwellian and b) x-form for
  - Probes (solid)
  - OES (open)
  - ‘global’ model (line)
- Global model
  - Volume averaged
  - Particle balance – ionization rate must match wall losses



Conclusions: Non-Maxwellian EEDFS

- Non-Maxwellian EEDFs have been observed using Ar emissions for wide range of ICP conditions
  - sensitive to fairly subtle changes in EEDF
  - "*x*-form" of EEDF well suited for ICP
    - captures EEDF tail depletion

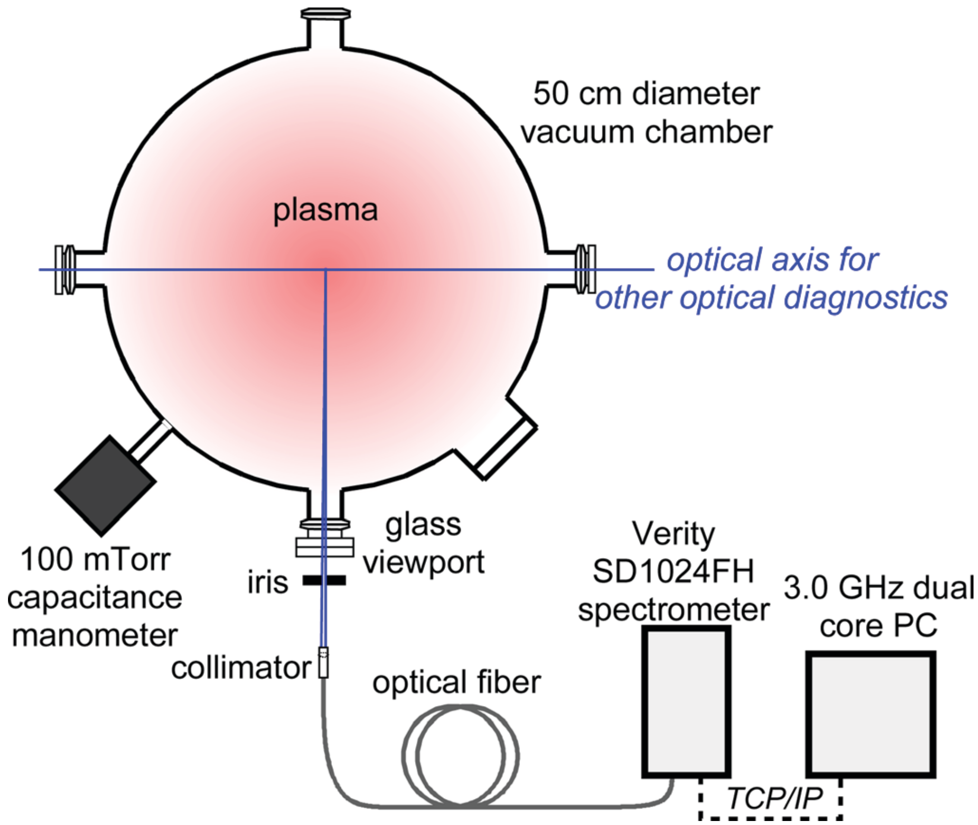
- OES - BF is a simpler alternative to absorption spectroscopy to determine $1s_y$ concentrations

- emission model must include contributions from:
  - excitation to higher lying states followed by cascade
  - excitation from metastable/resonance levels
  - reabsorption by metastable and resonance levels
  - electron-driven transfer between emitting levels closely spaced in energy
    - Bonus: allows determination of electron density n_e

Real-time monitor of plasma conditions: time-varying and pulse-modulated ICP

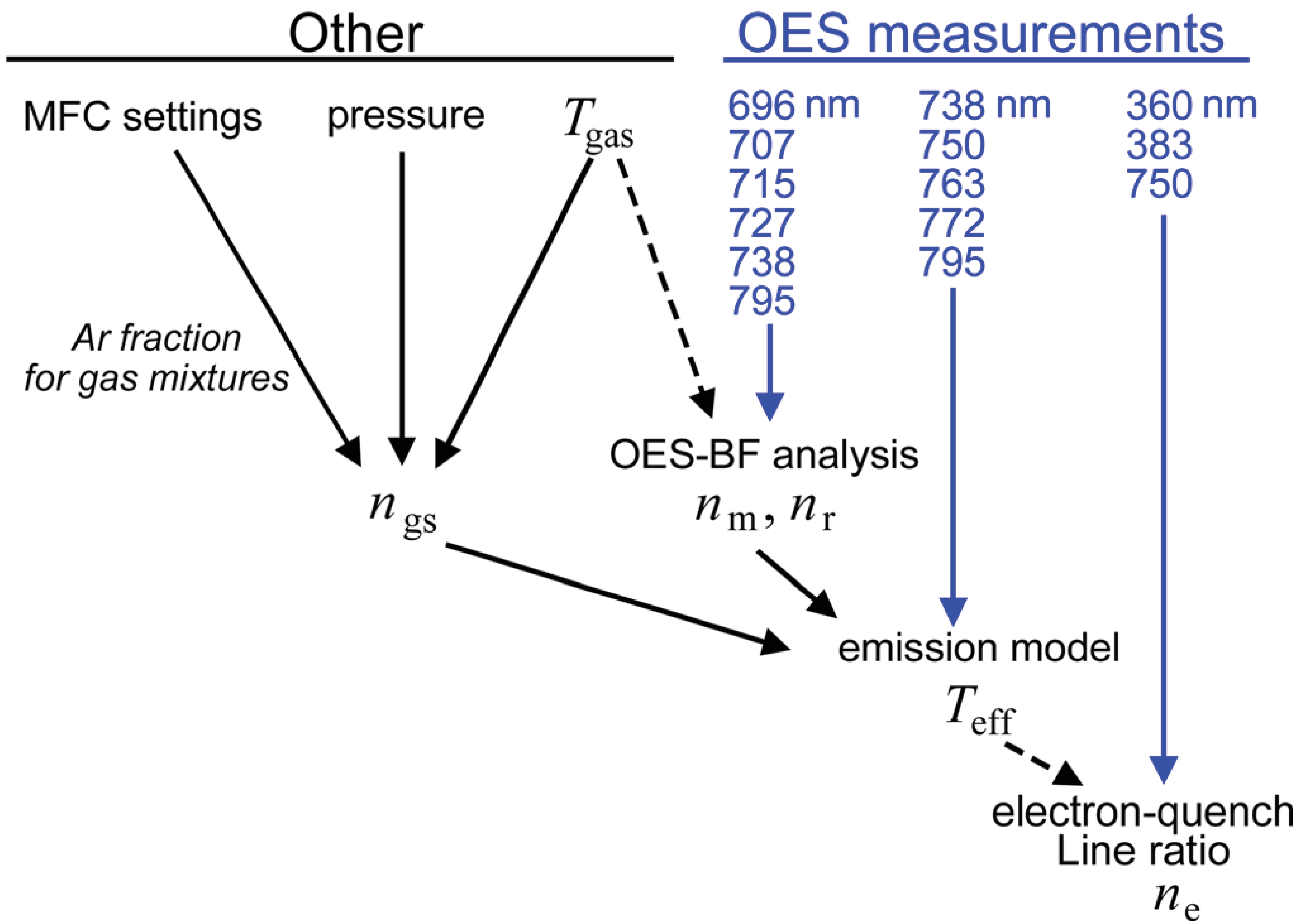
OES plasma diagnostics in real time

- Verity spectrograph
  - fast spectra acquisition
  - compact
  - low-resolution (~1 nm) spectra (200-800 nm)
  - similar to systems often included on plasma process equipment



JVSTA 021303, 2013

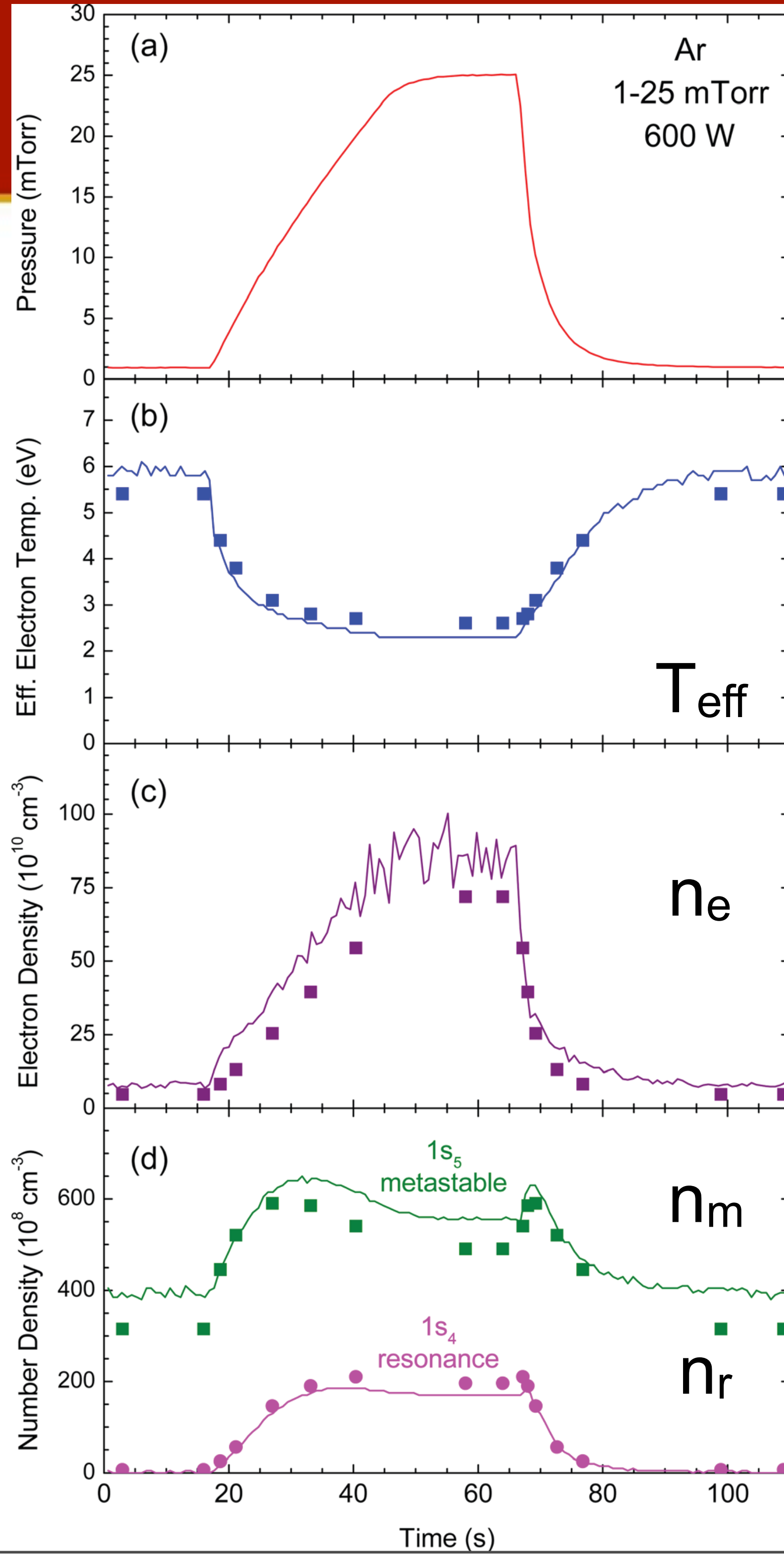
Flow chart for real time measurements



Pure Ar: real time/ pressure varied

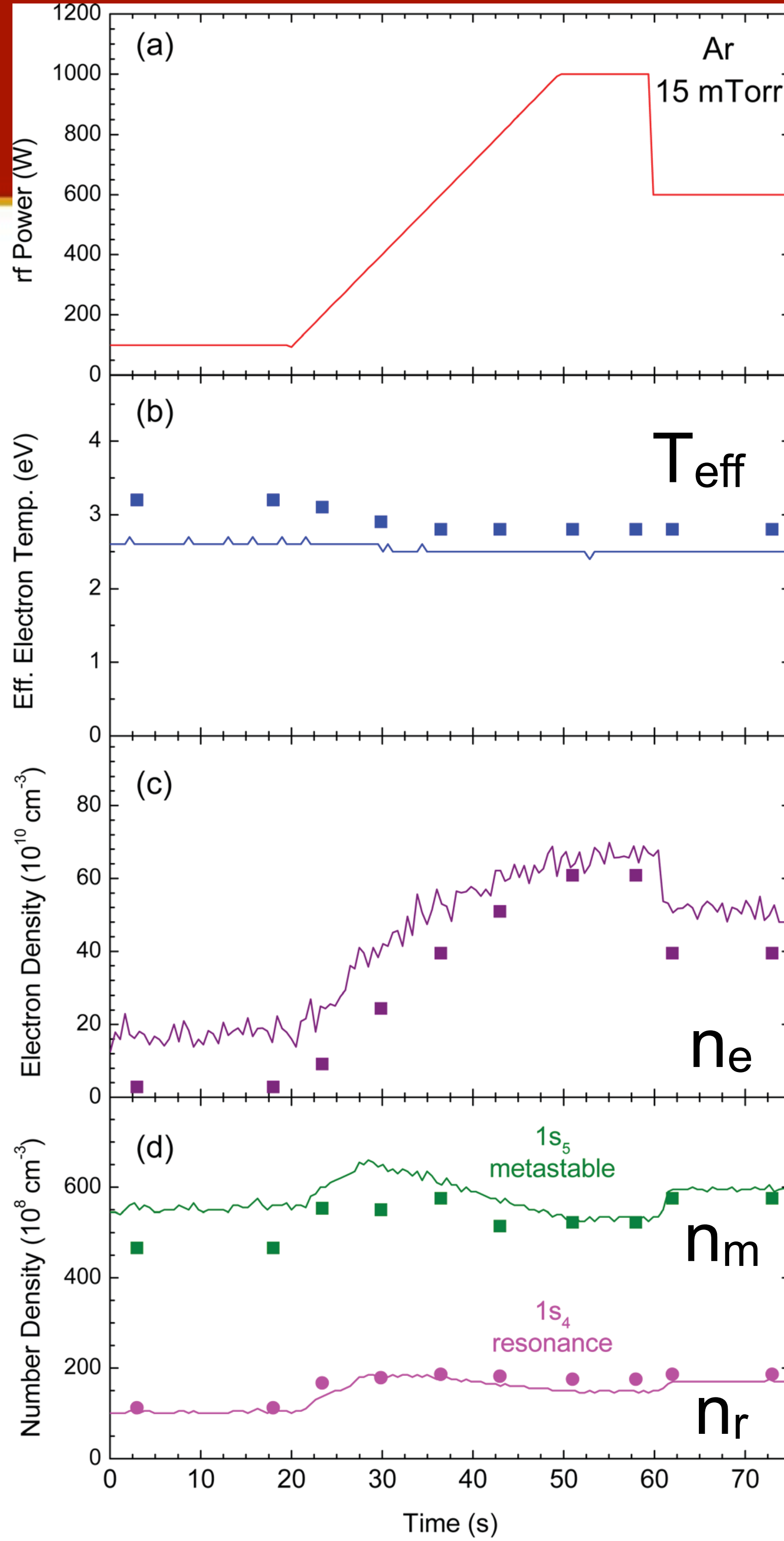
- Computer controlled time-varying Ar *pressure;* power held fixed at 600 watts
- plasma parameters evolve in time in response to pressure change

- solid lines show instantaneous measurements vs. time
- dots are static measurements made with the same parameter settings



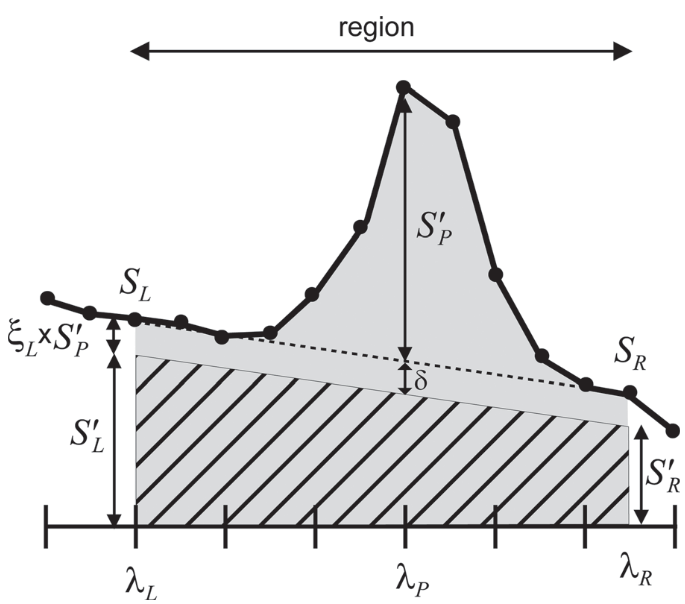
Pure Ar: real-time/ power varied

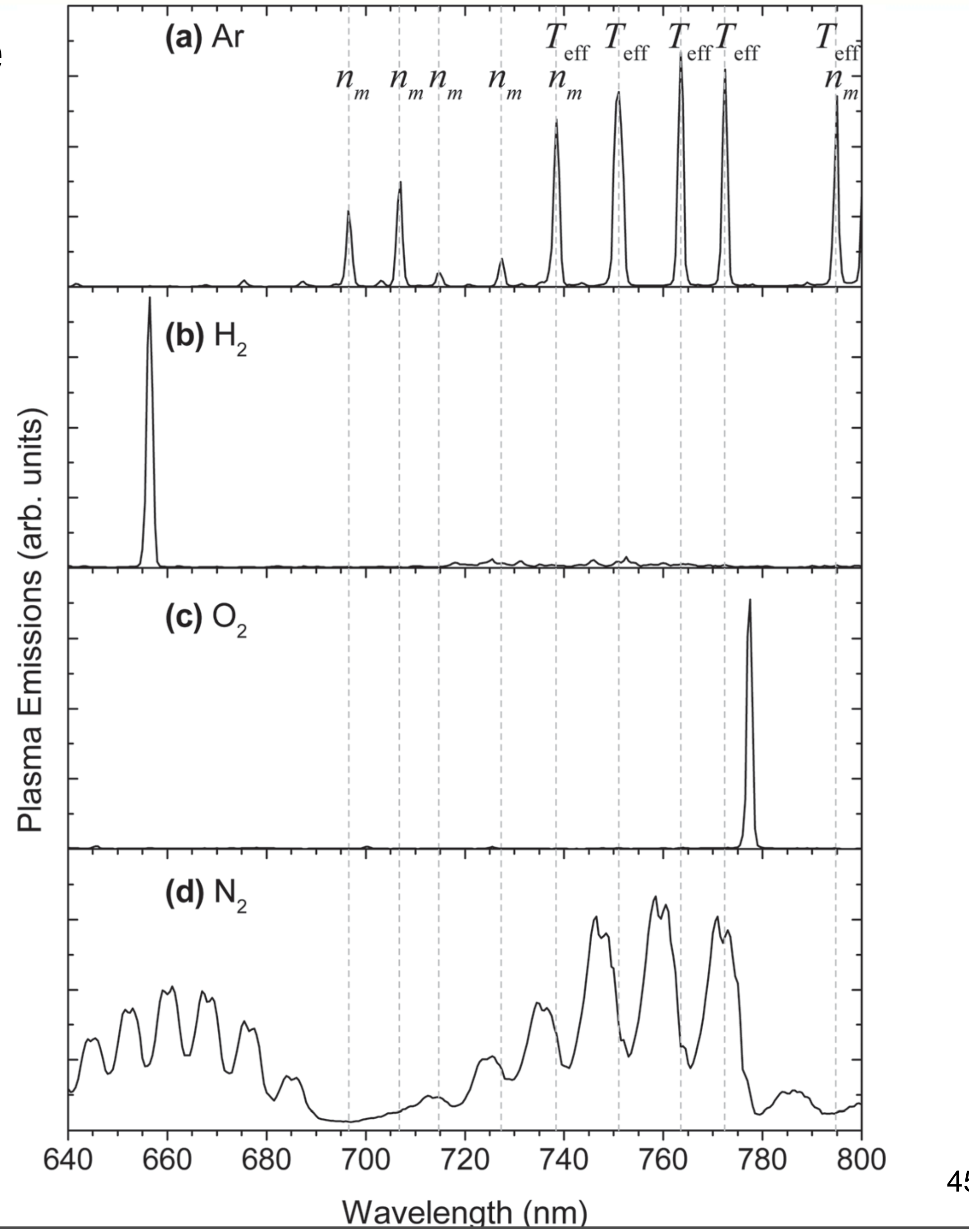
- Computer controlled time-varying Ar *power;* pressure held fixed at 15 mTorr
- plasma parameters evolve in time in response to pressure change



OES plasma diagnostics: gas mixtures

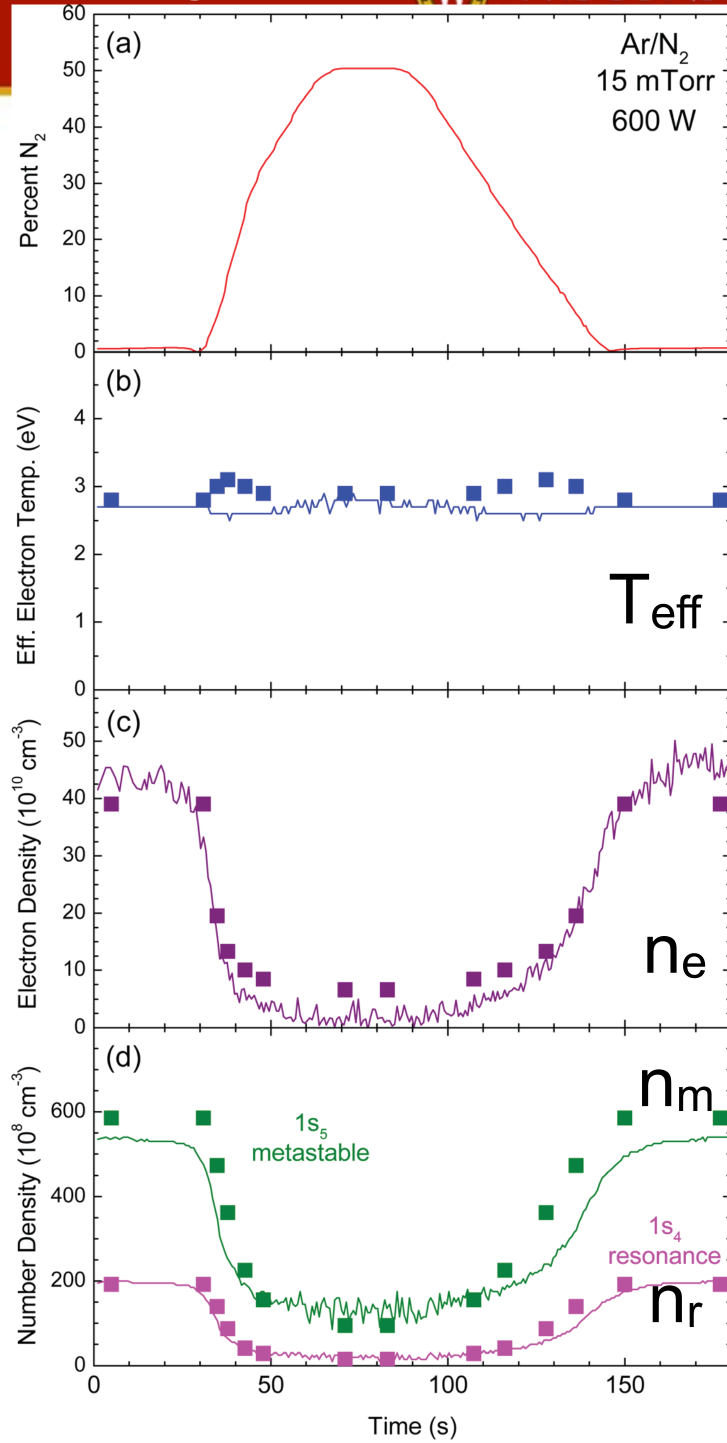
- Challenge: difficult to separate OES lines
  - from neighboring Ar lines
  - from molecular OES features





OES plasma diagnostics in real time

- Computer controlled Ar and N_2 flow rates; pressure held fixed at 15 mTorr, power at 600 W



Detection of VUV in argon-containing ICP

Overview

- VUV flux to wafer matters in plasma processing for integrated circuit manufacturing (and other applications!)

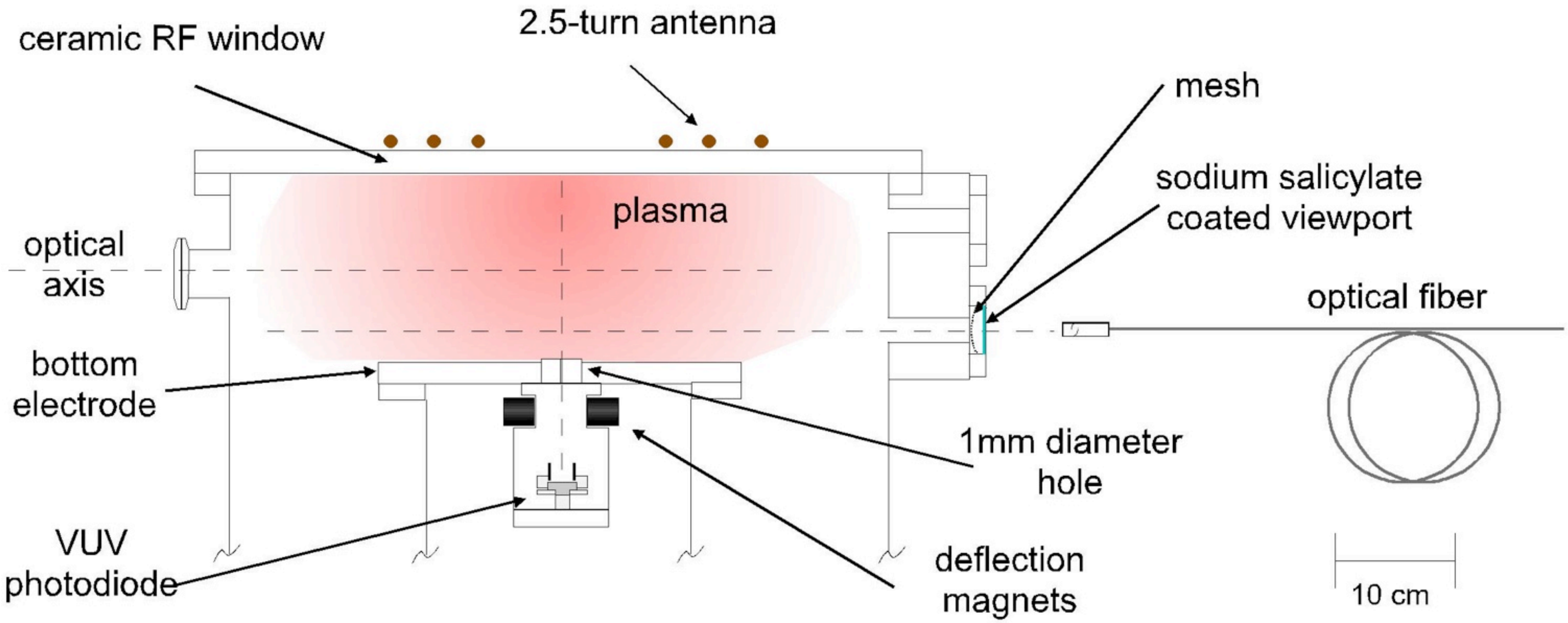
- Diagnostic challenge: no way to non-invasively measure VUV flux directly
  - VUV is *not* transmitted by windows or air

- In Ar containing plasmas, VUV is emitted by resonance level atoms. We posed the following question: can non-invasive measurements of n_r serve as a proxy for VUV?

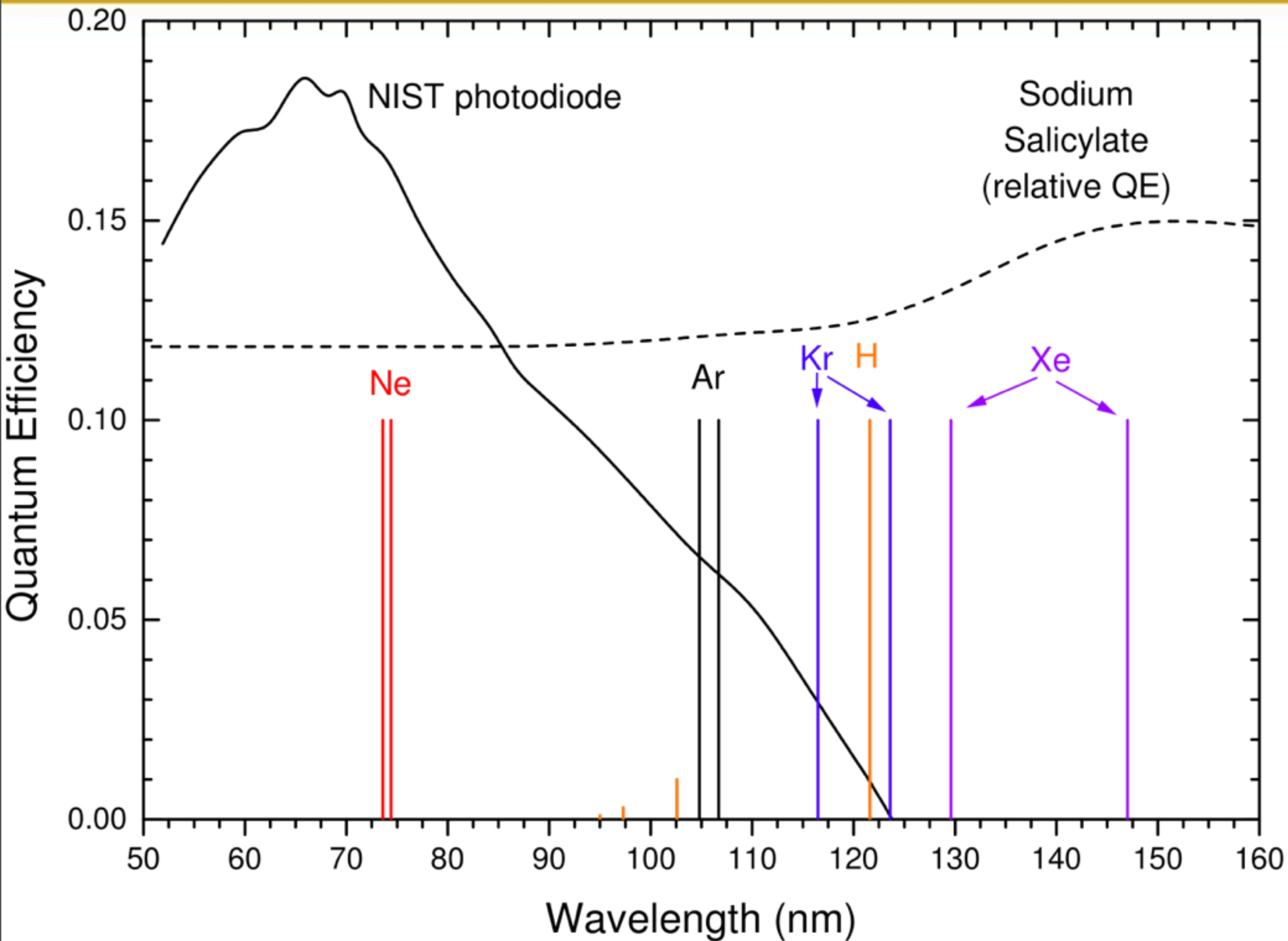
- Experimental evidence indicates the answer is a *qualified* "yes"…

VUV Photon Flux Detection – 2 methods

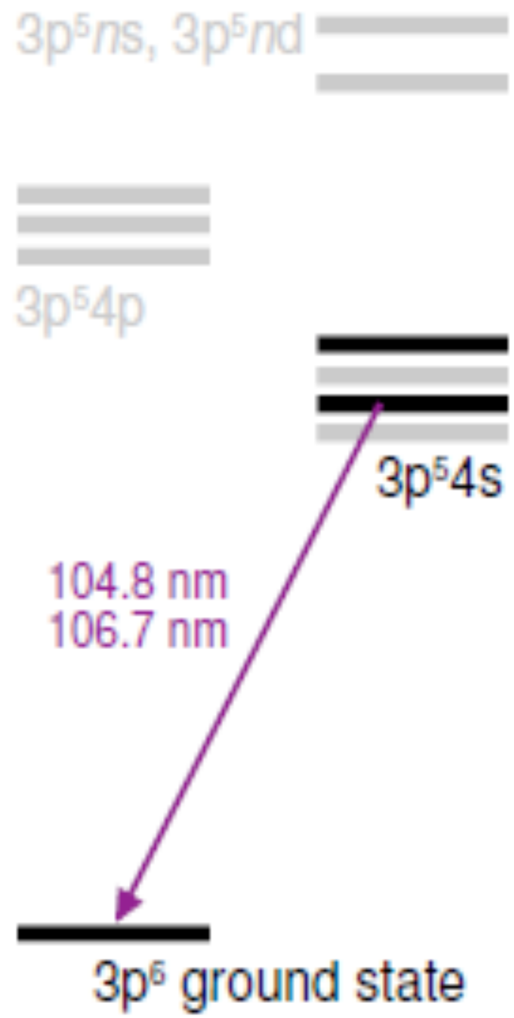
- Windowless NIST photodiode installed below ground electrode
- Relative VUV flux detected through visible fluorescence from sodium salicylate coated viewport



Sodium salicylate signal: sensitive at wavelengths beyond photodiode limit



Ar energy levels

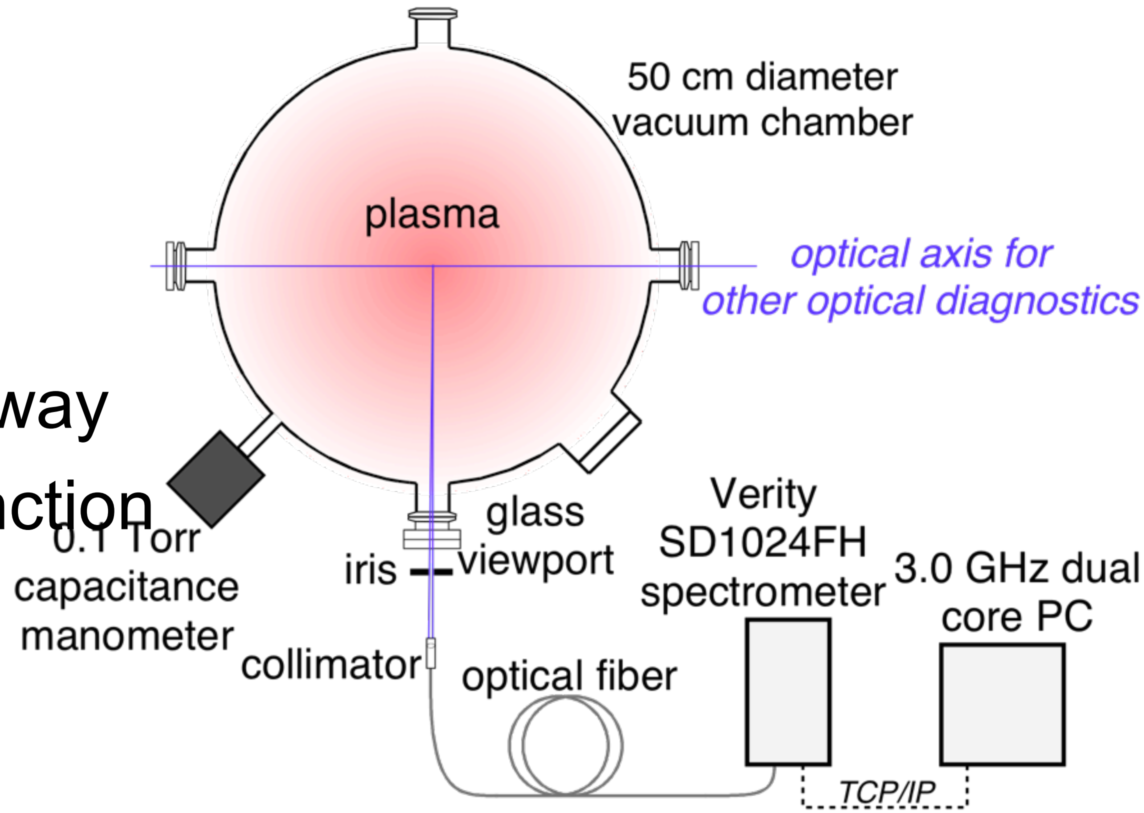


Due to *different* wavelength dependent sensitivities, relative signal strengths for photodiode and sodium salicylate vary with gas type

Non-invasive measurement of resonance level density

Branching Fraction

- Intensity ratios *altered* by reabsorption in quantifiable way
- Reabsorption is a known function of resonant level density



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Radiation model predicts VUV signal

- Model elements
  - Local VUV emission is proportional to resonance density
  - Chance of emitted photon reaching VUV photodiode depends on:
    - Geometry – line of sight through pinhole
    - Reabsorption – “escape factor” depends on $n_{gas}=p/kT_{gas}$, thus:
      - Gas pressure, p
      - Gas temperature, T_{gas}
- Both photodiode signal and VUV flux to walls calculated

Non-invasive measurement of gas temperature

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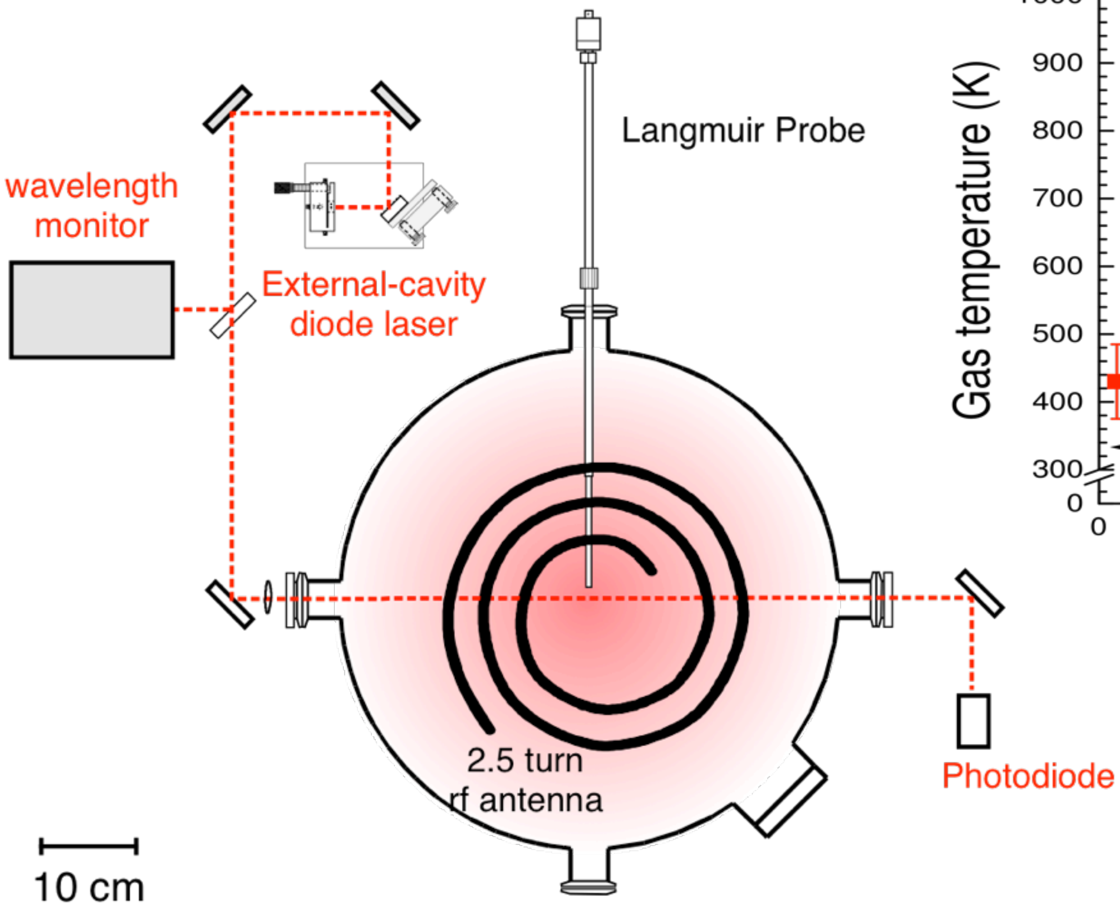
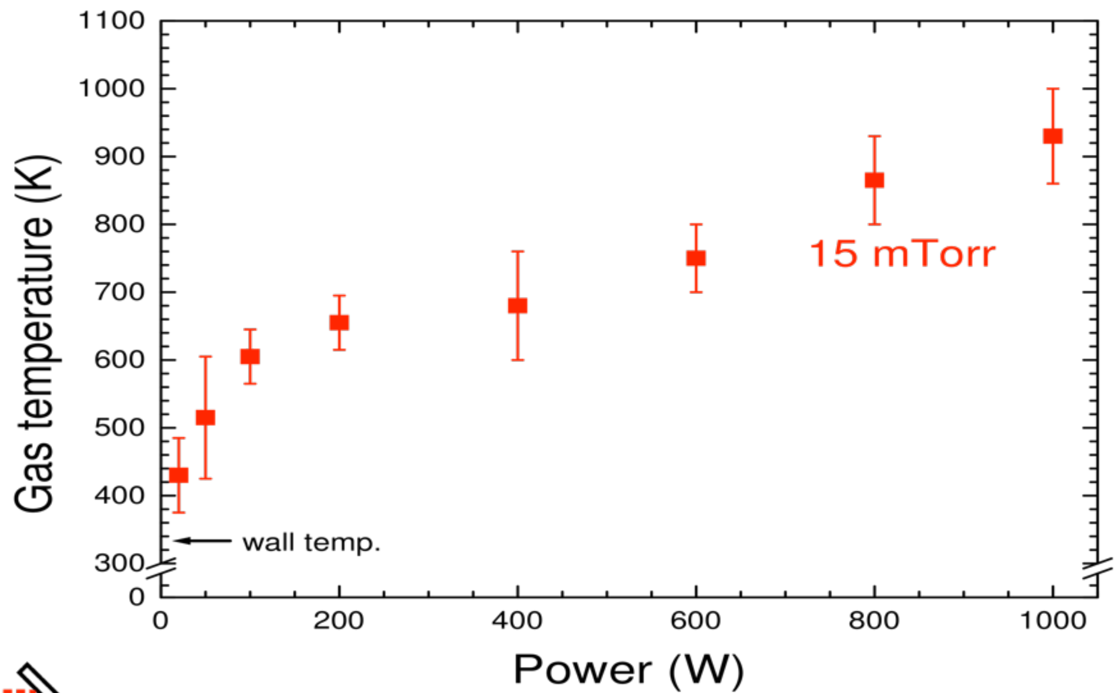
Diode laser absorption



T_{gas} varies significantly

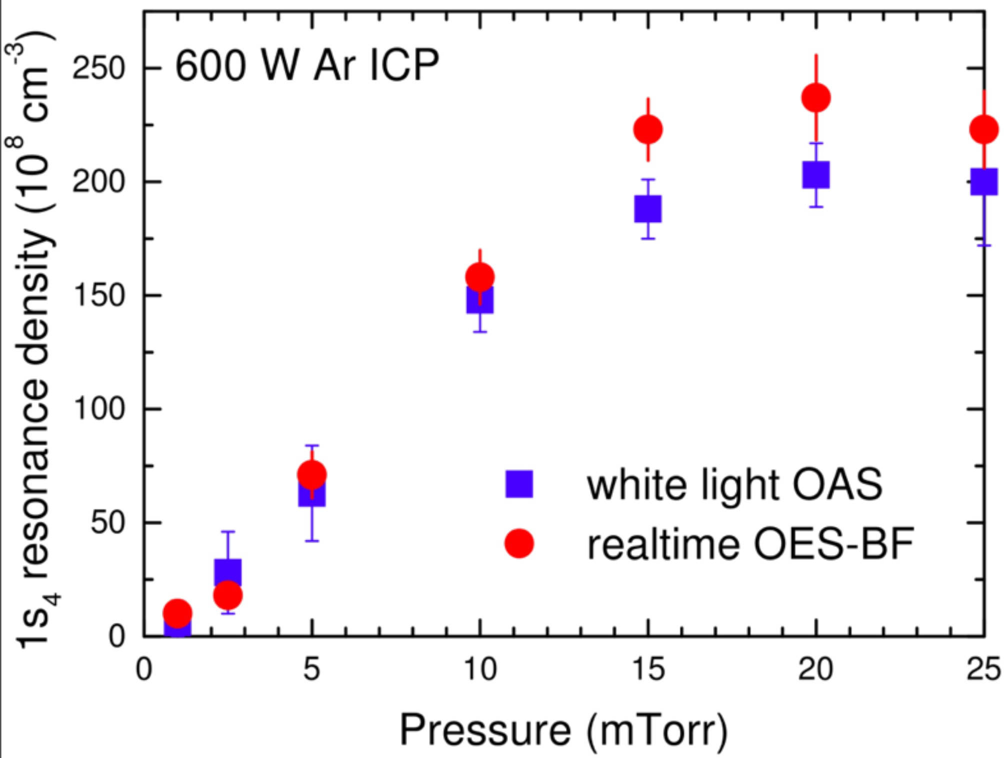


Ground state atoms reabsorb VUV

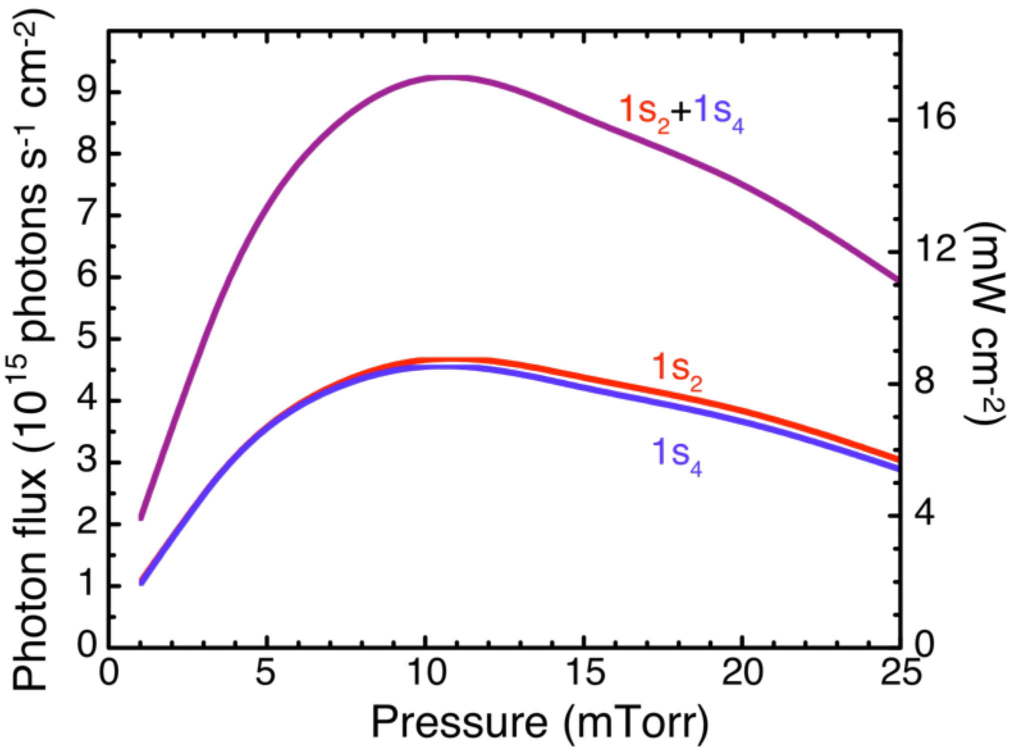
Gas density $n = p/kT_{gas}$ decreases as T_{gas} increases

Pressure scan - Ar

Resonance density



VUV (predicted by model)

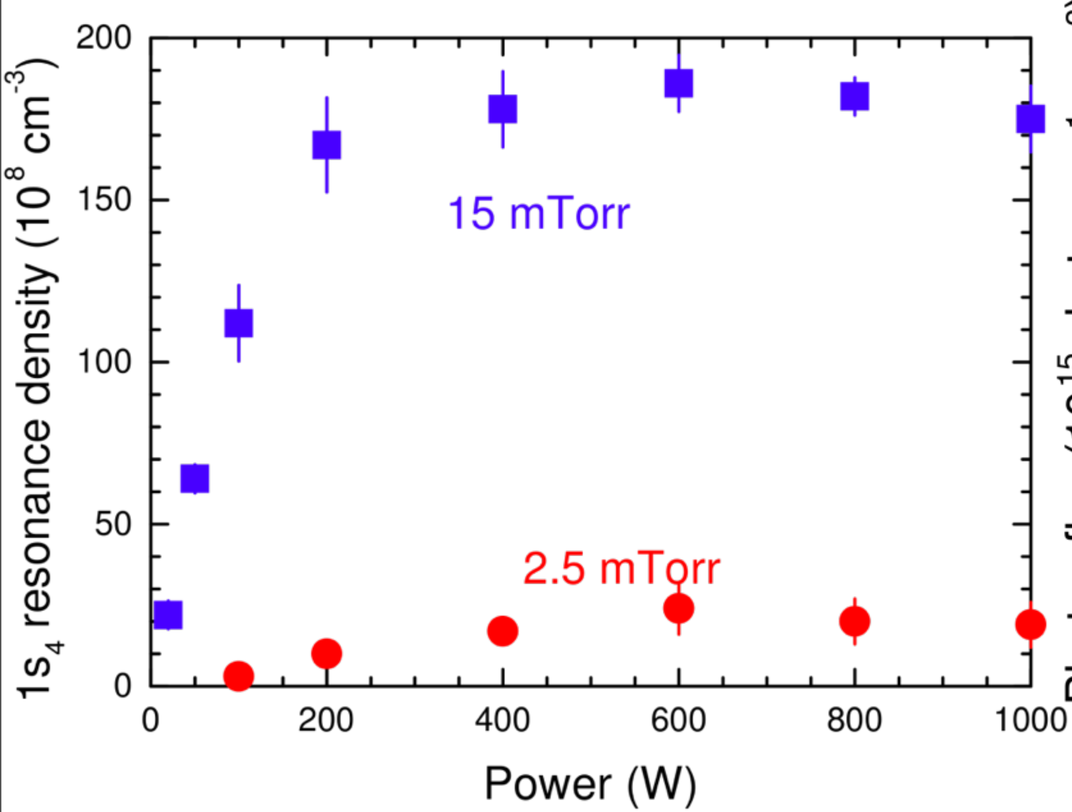


VUV flux decreases with pressure due to enhanced reabsorption.

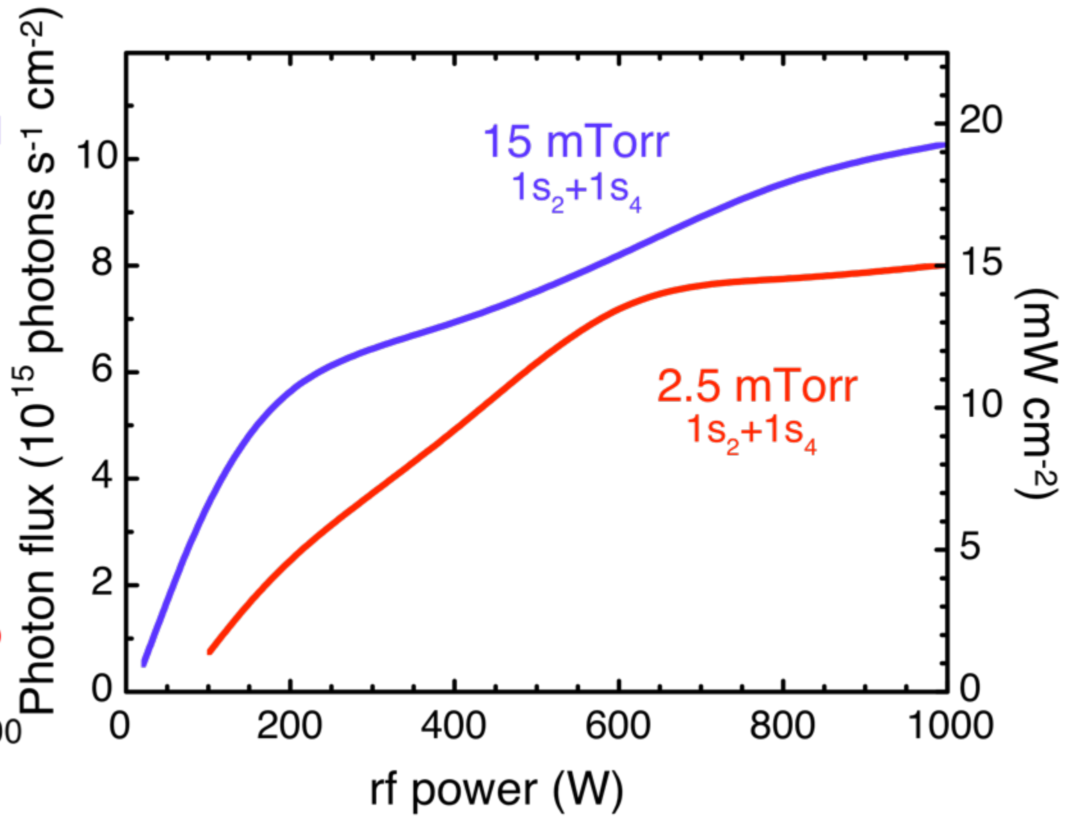
JVSTA, 021304, 2014

Power scan - Ar

Resonance density

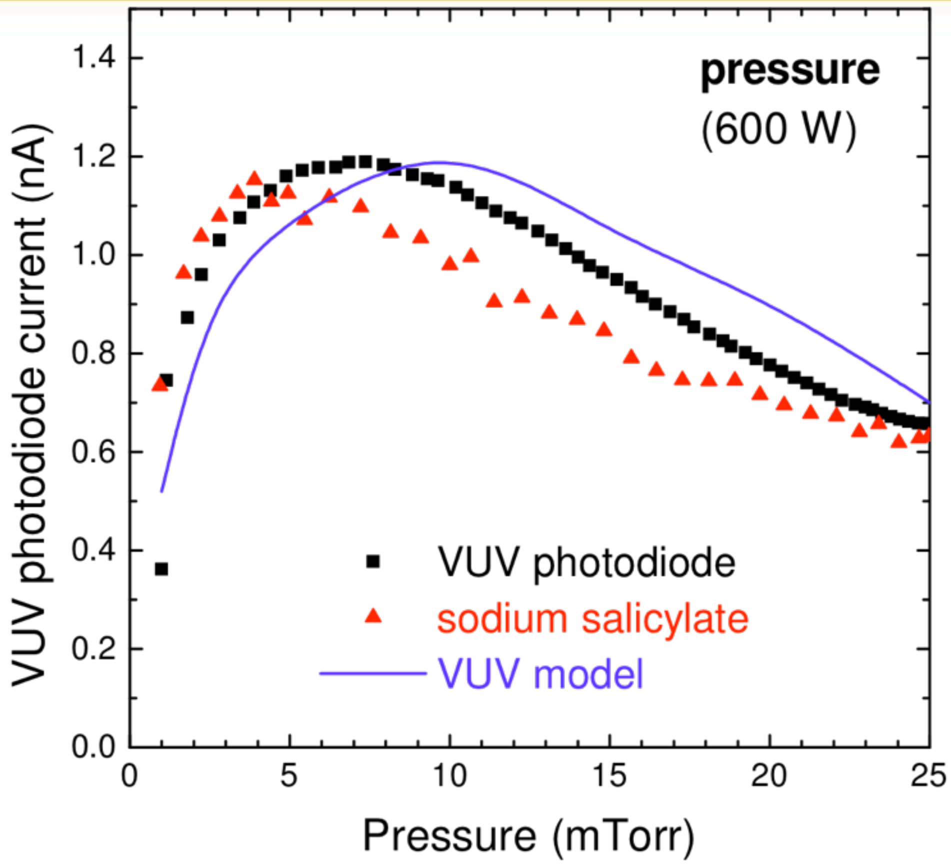


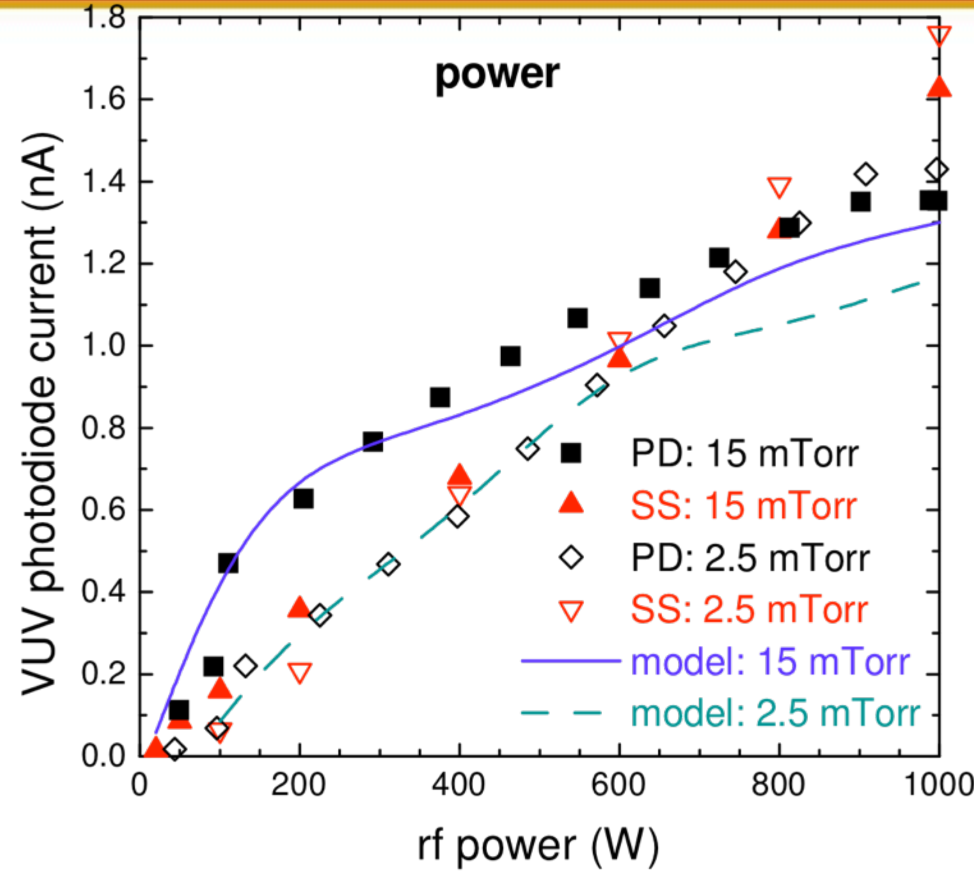
VUV prediction



VUV flux increases with increasing power – rarefaction leads to diminished reabsorption.

VUV photon flux in Ar ICP from photodiode and sodium salicylate agree with model



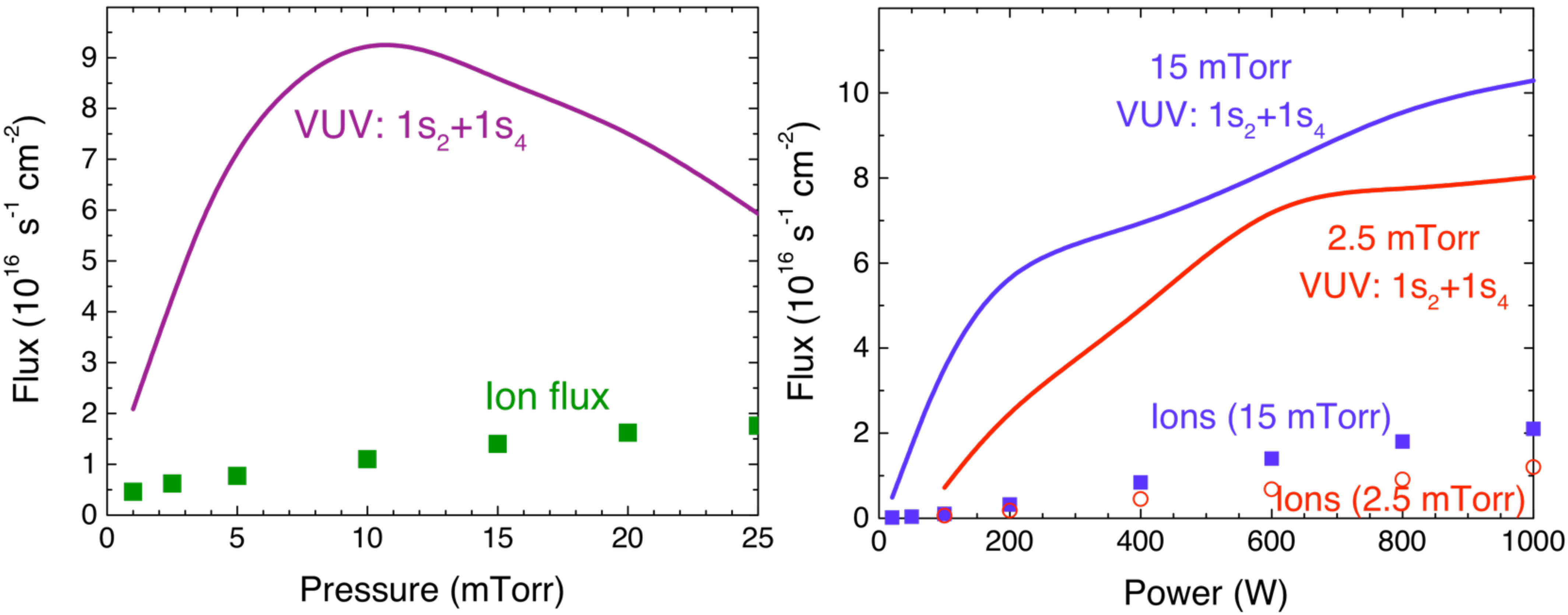


- At higher pressures, radiation reabsorption increases due to increased ground state atom concentration.

- At constant pressure, VUV photon flux increases with power when excited state densities increase.

- Model is in accord with photodiode and sodium salicylate data

VUV *flux* at electrode location



VUV photon flux is greater than ion flux for all conditions

Ar/N_2 plasmas - Ar model works due to no N_2 emissions in VUV range

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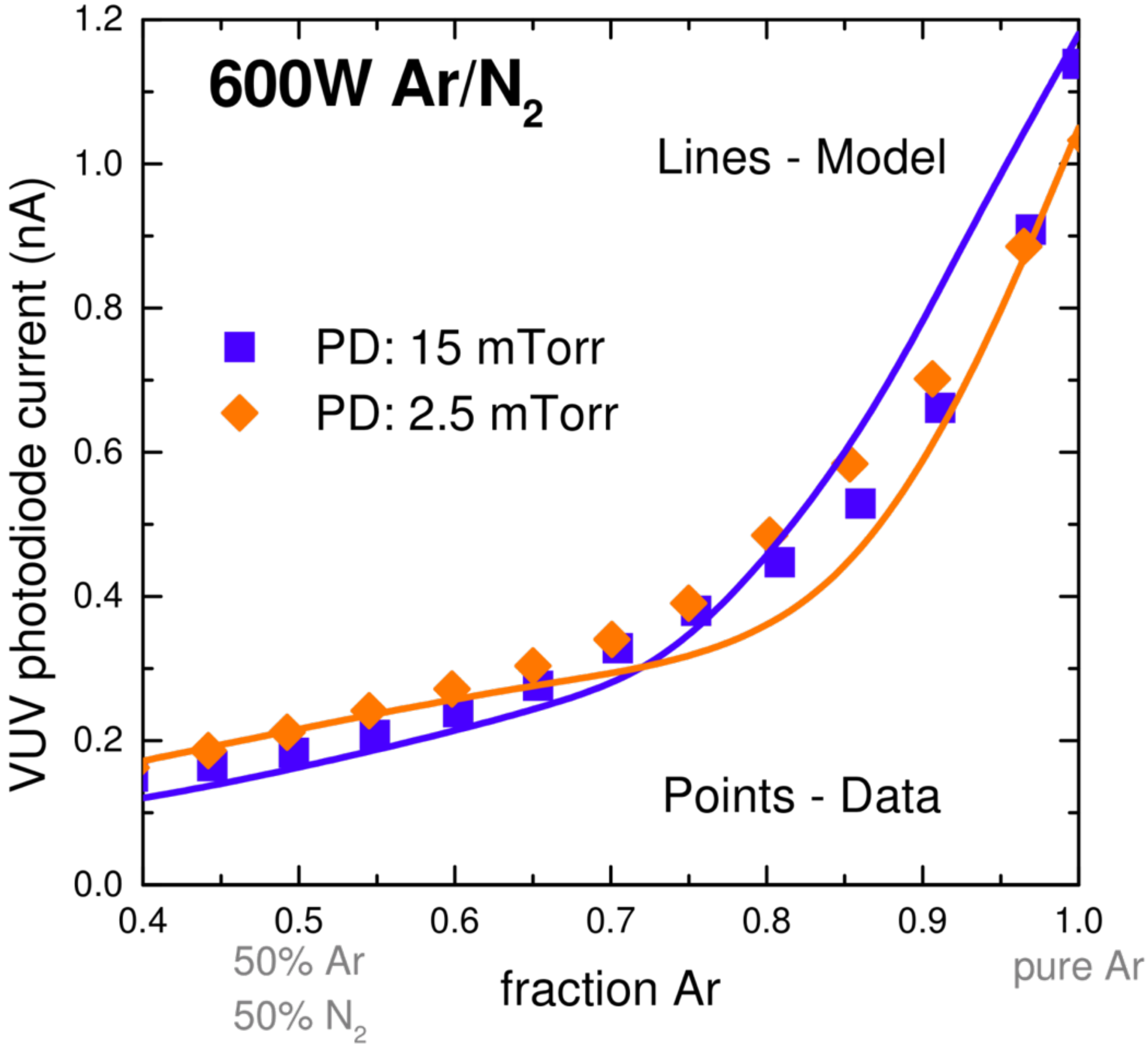

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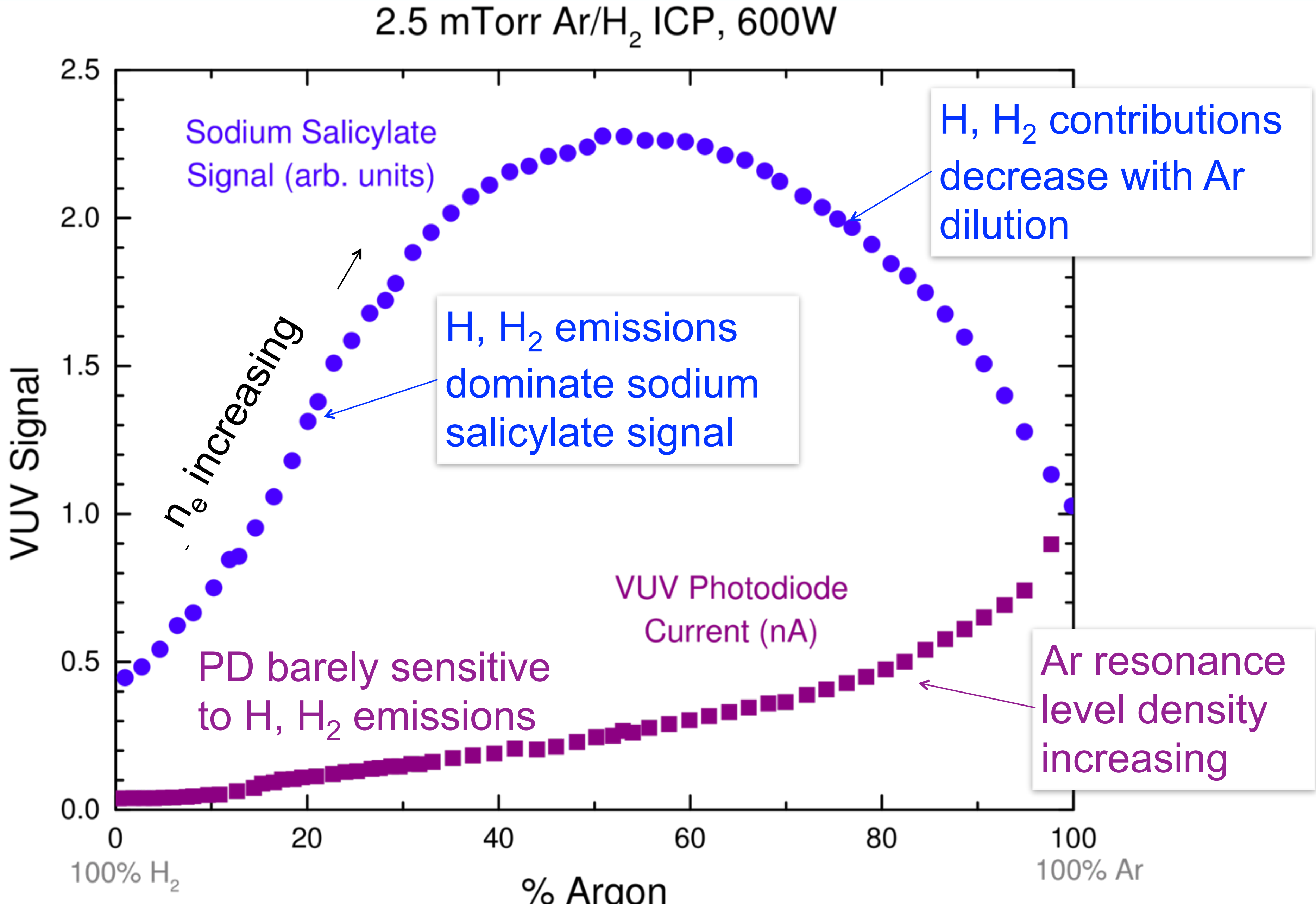
For Ar/H_2, H, H_2 VUV (90-180 nm) emissions *add* to Ar signals at 104.8 &106.7 nm



JVSTA, March/April 2015

VUV: concluding remarks

- Non-invasive VUV detection has been demonstrated
- A radiation model has been developed to infer VUV fluxes:
  - Inputs: measured resonance level density, Ar pressure, gas temperature
  - The model accounts for VUV reabsorption in plasma
- VUV fluxes from model in Ar agree with direct measurements using
  - VUV photodiode
  - Sodium salicylate fluorescence
- For Ar/N_2 mixture, the model works well because only Ar contributes to VUV emissions
- For Ar/H_2 mixture, H and H_2 contribute to VUV emissions – relative contributions inferred by combining Ar model and sodium salicylate measurements

Summary

- OES offers a promising approach to plasma characterization
  - Non-Maxwellian EEDFs, electron density and effective temperature
  - metastable concentrations
  - real-time plasma parameters
  - VUV
  - method is
    - non-invasive
    - applicable in rare gas containing plasmas
    - applicable in conditions where Langmuir probes impractical

- Successfully applied to low-pressure ICP - what about higher pressure?