Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Study of optical emission spectroscopy in dual frequency synchronized pulsed capacitively coupled discharges with DC bias at low-pressure in $Ar/O_2/C_4F_8$ plasma etching process

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T. Gohira, Y. Ohya, O. Noriyasu and M. Hori

Plan of the presentation

- **Motivation for the present OES study**
- **Formulation of the present work**
  - ✓ Determination of deviation of plasma from LTE
  - ✓ Mathematical formulation to evaluate T_e
  - ✓ Determination of T_e and validity of corona balance
- **Computations of electron impact excitation rate coefficients**
- **Experimental results and discussion (T_e evaluation)**
  - ✓ Boltzmann Plot: Excitation temperature: T_{ex}
  - ✓ Modified Boltzmann equation: Electron temperature: T_e
  - ✓ Variation of T_e with RF pulse condition
- **Determination of plasma density (n_e evaluation)**
  - Formulation of equation for n_e
  - Variation of n_e with RF pulse condition
  - Validation of our result by RF compensated Langmuir probe
- **Summary/Conclusion**
  - ✓ Scientific aspects

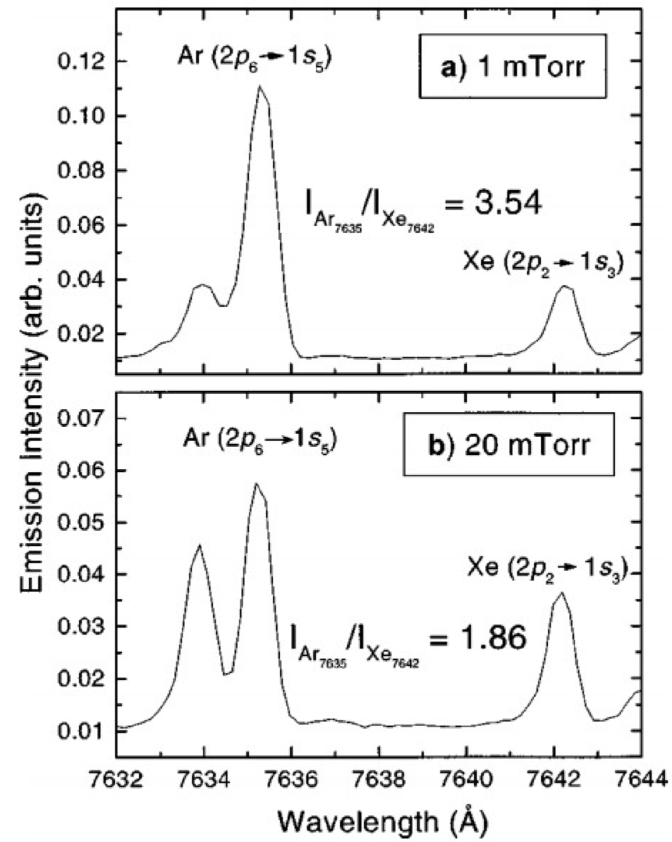
Motivation for the present OES study

Motivation for the present OES study: T_e evaluation

- OES is a non-intrusive diagnostic method. One can get information about plasma parameters, excited species, etc.
- Many reported works have used the mixed gas of Ar/He/Xe/Kr and the approach of trace of rare gas (TRG) for the estimation of electron temperature (T_e) from the ratio of line intensities during the OES diagnostic. However, in the actual plasma process experiment the experimental gas contains no mixed gas of Ar/He/Ne/Xe.

Sometimes, the partial pressure of mixed gases become considerable with respect to the experimental gas for the etching or deposition process.

The plasma condition and hence, the plasma parameters would be different during the plasma diagnostics and actual plasma process.



PRE 60, 6016 (1999); J. Vac. Sci. Technol. A. 20, 555 (2002)

Motivation for the present OES study: T_e evaluation

- In other method, researchers have used kinetic approach using collisional-radiative (CR) model for low-pressure N_2[2] plasmas and Ar/Ne[3] plasmas, and solve the rate balance equation using collisional-radiative (CR) model to solve for T_e and n_e.

- Note that the rate or excitation coefficients involved in the rate balance equations [2-4] used for the estimation of T_e and n_e are function of the gas temperature T_g. However, the evaluation of T_g at low-pressure plasma is not straight forward, which needs N_2 gas mixing for getting the N_2 emissions[5] or additional methods like laser-induced fluorescence (LIF)[6] and Fabry–Perot Interferometry[7].

- Some studies in Ar/Ne plasmas, the line intensity ratios are used to determine the value of T_e.

- Thus, at low-pressure, there is no straight forward and simplified method using OES of Ar containing plasmas to determine T_e in non-equilibrium plasmas.

[2] Plasma Sources Sci. Technol. 17, 024002 (2008); [3] J. Phys. D: Appl. Phys. 42, 025203 (2009);
[4] Resource Eff. Technol. 3, 187 (2017), [5] J. Phys. D: Appl. Phys. 40, 1022 (2007); [6] Plasma Sources Sci. Technol. 23 023001 (2014) review paper by Bruggeman. [7] B. Xu, Y. M. Liu, D. N. Wang, and J. Q. Li, "Fiber Fabry–Pérot Interferometer for Measurement of Gas Pressure and Temperature," J. Lightwave Technol. 34, 4920-4925 (2016)

Motivation for the present OES study: T_e evaluation

- Considerable work in the literature has also been done at very high pressures and/or atmospheric pressures. Such discharges, assume the condition of partial local thermal equilibrium (LTE) that approximate the electron excitation temperature $T_{ex} \sim T_e$ using Boltmann plot.[8-10]

- At low-pressure and low-to-moderate density plasmas, the excited atomic/ionic densities are not in Boltzmann equilibrium; that is, excitation and de-excitation are not controlled by collisions with electrons. In such cases, the use of Boltzmann plot only provides T_{ex} and not the T_e.

- In glow discharges, at low-pressure with low-neutral density (~10^{13}-10^{15} cm^{-3}) and low-to moderate electron density (~10^{8}-10^{12} cm^{-3}), multi-step ionization would be important. Accordingly, with increasing electron density (n_e), multi-step excitation of the metastable level $1s_5$ via the excited Ar and resonant states $1s_2$, $1s_3$ and $1s_4$ could be dominant [10]. However, at low electron densities and pressures (a few Pa), the formation of $1s_5$ can predominantly occurs from the ground state Ar by direct excitation.

[8] Surf. Coat. Technol. 364, 63 (2019); [9] J. Anal. At. Spectrom. 32, 782 (2017); [10] POP 17, 103501 (2010) (Prof. Choe's paper), [11] J. Phys. D: Appl. Phys. 35, 1777 (2002)

Motivation for the present OES study: T_e evaluation

- Earlier plasma density measurements[12, 13] by surface wave probe (in our center's work) have shown an overall plasma/electron density (n_e) variation in the range of ~ 10^{10} -10^{11} cm^{-3} at a low discharge power.
- Due to the low electron densities ~ 10^{10} -10^{11} cm^{-3} (our center's work), it is possible that direct excitation from the ground state along with radiative decay can be the dominant mechanisms.
- Thus, the direct excitation[14] mechanism will control the generation and destruction of excited levels, hence, a corona balance could drive the plasma kinetics in our experiments.
- We need to validate the corona balance formalism proposed by Fujimoto[15] relevant to our experiment and plasma parameters.
- Thus, T_e can be determined using Ar emissions straight forward from the OES emission lines. Also, we can determine electron density by combining Saha and Maxwell-Boltzmann equations.
- Simultaneous determination of both T_e and n_e will provide better insight of the etching processes along with the capability of plasma sources.

[12] Jpn. J. Appl. Phys. 55, 080309 (2016). [13] J. Phys. D. 50, 155201 (2017);
[14] Phys. Rep. 191, 109 (1990); [15] J. Phys. Soc. Japan 47, 273 (1979).

Formulation of the present work

- **Determination of deviation of plasma from LTE**
- **Mathematical formulation to evaluate T_e**
- **Determination of T_e and validity of corona balance**

Description of macroscopic/microscopic state of plasma

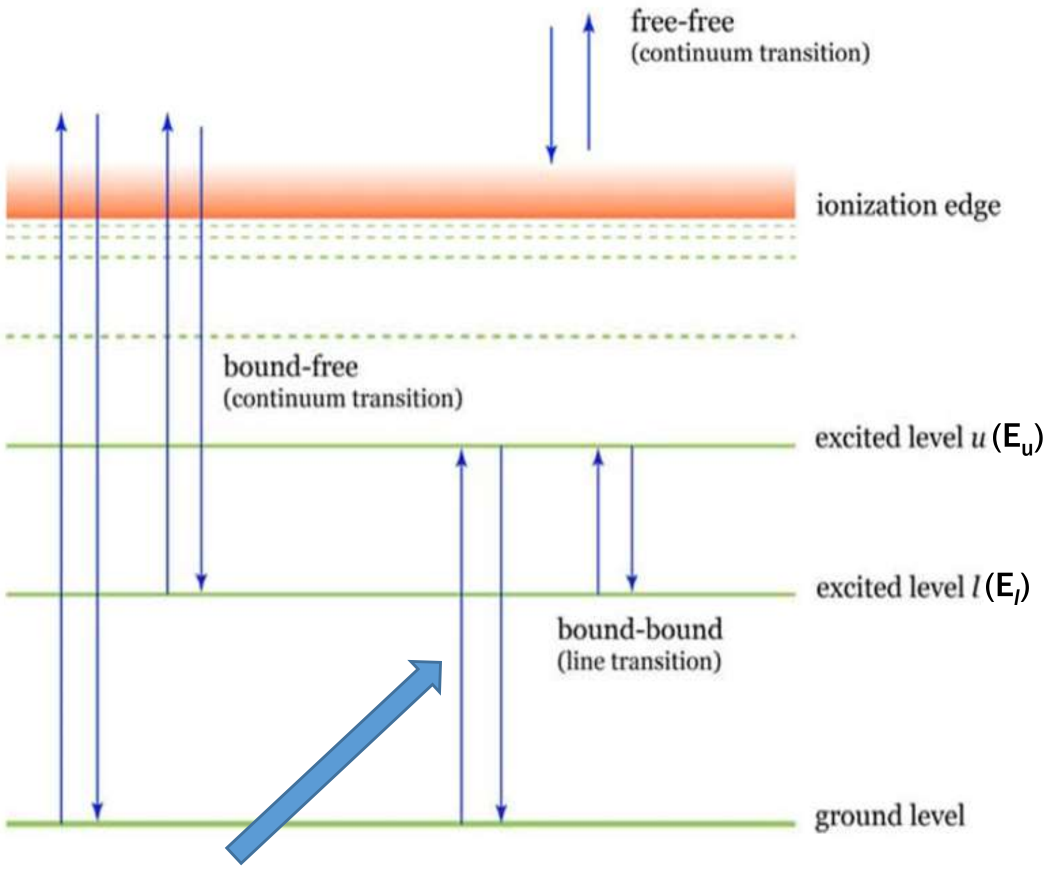
- Velocity distribution: by Maxwell Equation
- The excited state distribution: by Boltzmann Equation
- The relation between the densities of ionic states: by Saha Equation
- The distribution of the photon gas: by Planck's radiation law.

✓ In thermodynamic equilibrium
- ❑ All these distributions are characterized by the same temperature.
- ❑ Every detailed microscopic process is balanced by its inverse process.

Various microscopic processes occur in plasmas during process

Nature of balance	Reaction scenario in the plasmas	Physical situation
Maxwell balance	$X+Y \leftrightarrow X+Y$ $E_X+E_Y=(E_X-\Delta E)+(E_Y+\Delta E)$	Kinetic energy exchange (ΔE) and conservation
Boltzmann balance	$X+A_l+E_{\text{internal energy}} \leftrightarrow X+A_u$ A_l = atom in a lower state *l*	De-excitation $\leftarrow$ $\rightarrow$ Excitation
Saha balance	$X+A_p+\lvert E_p\rvert \leftrightarrow X+A_l^{+}+e$ *E*p = ionization energy of atom A_p = atom in state p	Recombination $\leftarrow$ $\rightarrow$ ionization
Plank balance	$A_u \leftrightarrow A_l+h\nu$ $A_u+h\nu \leftrightarrow A_l+2h\nu$	Absorption $\leftarrow$ $\rightarrow$ Spontaneous emission Absorption $\leftarrow$ $\rightarrow$ Stimulated emission

Formulation of work



Direct excitation from ground state

Absorption:
Upper energy level: $h\nu + E_l \rightarrow E_u$

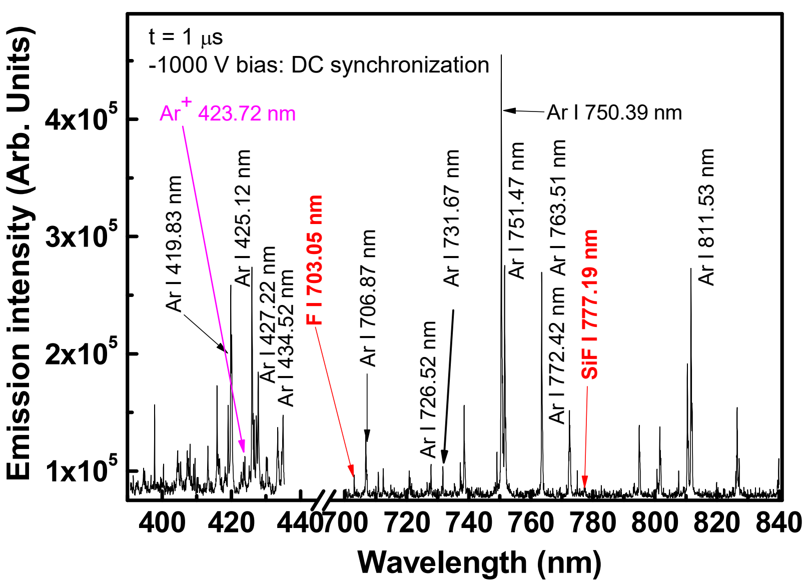
Spontaneous Emission:
From upper energy level:
$E_u \rightarrow E_l + h\nu$

Stimulated Emission:
From upper energy level:
$h\nu + E_u \rightarrow E_l + 2h\nu$

To apply the conventional Boltzmann plot,
we consider (assume) the upper excited energy levels of the selected (observed in our experiments) transition are in LTE. This suggests that the population density of such energy levels follow the Boltzmann equation.

OES diagnostics: Typical spectrum in our discharge

Observed dominant emissions from Ar lines



The excitation temperature (T_{ex}) can give the first estimation of T_e in the low pressure Ar rich/O_2/C_4F_8 plasma.

T_{ex} can be determined as

$$ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) = \frac{E_u}{k_B T_{ex}} + \text{Constant} \qquad (1)$$

$$\Rightarrow \frac{E_u}{k_B T_{ex}} = ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) + C_1$$

where

I_{ul} = Emission intensity (in arb. Unit) of the emission between the upper energy levels u and the lower energy level l

g_u= Statistical weight of emitting level u relevant to the transition u $\rightarrow$ l

A_{ul} = transition probability in s^{-1} corresponding to the radiative emissions

E_u = Excitation energy (eV) of upper level u

k_B = Boltzmann constant

C_1 = Constant

Spectrum acquired for the operation condition:
With synchronization (time t = 1 μs)
DC bias = -300 V (RF on)
= -1000 V (RF off)

[8] Surf. Coat. Technol. 364, 63 (2019)
[9] J. Anal. At. Spectrom. 32, 782 (2017)

Table I: Spectroscopic data and parameters

λ_{ul} (nm)	E_u (eV)	g_u	A_{ul} (10^7 s^{-1})	Transition levels $E_u \rightarrow E_l$	p_u	f_{lu}
419.83	14.58	1	0.257	$5p[1/2]_0 \rightarrow 4s[3/2]_1^0$	3.395	2.26×10^{-3}
425.12	14.46	3	0.0111	$5p[1/2]_1 \rightarrow 4s[3/2]_2^0$	3.234	1.81×10^{-4}
427.22	14.52	3	0.0797	$5p[3/2]_1 \rightarrow 4s[3/2]_1^0$	3.312	2.18×10^{-3}
434.52	14.66	3	0.0297	$5p'[3/2]_1 \rightarrow 4s'[1/2]_1^0$	3.516	8.41×10^{-4}
706.87	14.84	5	0.20	$6s[3/2]_1^0 \rightarrow 4p[5/2]_2$	3.845	1.35×10^{-2}
726.52	14.86	3	0.017	$4d[3/2]_1^0 \rightarrow 4p[3/2]_1$	3.887	4.99×10^{-2}
731.67	15.02	3	0.096	$6s'[1/2]_1^0 \rightarrow 4p'[1/2]_1$	4.287	3.37×10^{-2}
750.39	13.48	1	4.450	$4p'[1/2]_0 \rightarrow 4s'[1/2]_1^0$	2.442	1.25×10^{-1}
751.47	13.27	1	4.020	$4p[1/2]_0 \rightarrow 4s[3/2]_1^0$	2.337	1.14×10^{-1}
763.51	13.17	5	2.452	$4p[3/2]_2 \rightarrow 4s[3/2]_2^0$	2.291	2.14×10^{-1}
772.42	13.33	3	1.170	$4p'[1/2]_1 \rightarrow 4s'[1/2]_0^0$	2.366	3.14×10^{-1}
811.53	13.08	7	3.310	$4p[5/2]_3 \rightarrow 4s[3/2]_2^0$	2.253	4.58×10^{-1}

Sources of error during estimation of $T_{ex} \neq T_e$

The main sources of error using Eqn. (1) for T_{ex} estimation arise from the inaccurate A_{lu} and acquired emission intensities I_{lu}. However, the use of logarithmic operation on the lhs shrinks the extent of error.

As an example: An error of 15 % in the argument of Eqn. (1) shrinks to $\rightarrow$ 2 % of error by the logarithmic operation

At low-pressure condition: The condition LTE is difficult to hold since the population density of excited (atom) states will not be in Boltzmann equilibrium.

↓

The excitation and de-excitation process might not be crucially controlled by electronic collisions

↓

T_{ex} will be different from T_e

↓

Thus, the fitted lines satisfying the Boltzmann equilibrium will not follow/overlap the data points

↓

Thus, there is departure/deviation of plasma from LTE

Determination of deviation of plasma from LTE

To know about the deviation of plasma from LTE and to determine T_e, we consider the formation of the effective principal quantum number p_u[14] for the excited states as

$$p_u = \sqrt{\frac{E_H}{E_{Ar} - E_u}} \qquad (2)$$

[14] Phys. Rep. 191, 109 (1990);

E_H = 13.6 eV, the Rydberg constant
E_{Ar} = 15.76 eV, the ionization energy of atomic species of Ar
E_u = Excitation energy (eV) of excited level u

The **Saha** equation (or equilibrium) describes the degree of ionization for any gas in thermal **equilibrium** as a function of the temperature, density, and ionization energies of the atoms

we further define the parameter $s_u(p_u)$

$$s_u(p_u) = \frac{N_u(p_u)}{N_u^s(p_u)} \qquad (3)$$

$N_u(p_u)$= population density of the excited state u
$N_u^s(p_u)$= population density of the excited state u in Saha Equilibrium

if $N_u(p_u) > N_u^s(p_u)$: $s_u(p_u) > 1$

When the excited states will be over populated, we can get this feature.

The density of energy level is larger than the value required to maintain Saha equilibrium.

The scenario suggests the plasma to be ionizing in nature

Determination of deviation of plasma from LTE

if $N_u(p_u)$, $N_u^s(p_u)$: $s_u(p_u) < 1$ ⇨ The scenario suggests the plasma can be of recombining in nature

- Note that the degree of ionization[19] at a low-pressure in RF plasmas is very small ~ $10^{-6} - 10^{-3}$ which corresponds to a very low ~ $10^{9} - 10^{11}$ cm^{-3}.
- The plasmas with low-electron density would make the coalitional process less effective than those with high electron density. This suggests the dominance of radiative processes.
- In the case of non-equilibrium plasmas with corona balance[14], there will be the balance between the populating and depopulating mechanism.
- The densities of excited states by the electron-impact excitation from the ground state can be termed as the populating mechanism, and the process of spontaneous emission can be thought as the depopulating mechanism.
- The corona balance process can be expressed as

$$n_e N_1 k_{1u}(p_u) = N_u(p_u) \sum_{u \rangle l} A_{ul} \qquad (4)$$

n_e = electron density; N_1 = Ground state population density
$k_{1u}(p_u)$= rate coefficient for electron impact excitation from the ground state 1 to excited level u; $N_u(p_u)$= population density of the excited state u

[19] Plasma Sources Sci. Technol. 10, 530 (2001)

Determination of deviation of plasma from LTE

- We consider an optical thin plasma in Eqn. (4) for all radiated emissions. The $N_u(p_u)$ can be determined for each relevant emission from level E_u

$$I_{ul} = \frac{h\nu_{ul}}{4\pi} A_{ul} N_u(p_u) L_{pl} \quad \Rightarrow N_u(p_u) = \frac{4\pi}{h} \frac{\lambda_{ul}}{c} \frac{I_{ul}}{A_{ul}} \frac{1}{L_{pl}} \qquad (5)$$

c = speed of light in vacuum;

L_{pl}= effective plasma length that emitted light radiation has to travel through

- We assume that the free electrons obey the Maxwellian EEDF so that we can express the rate coefficient $k_{1u}(p_u)$ for Ar as follows[20,21]:

$$k_{1u}(p_u) = 8.68\times10^{-8} c_{1u} Z_{eff}^{-3} f_{lu} \times \frac{u_a^{3/2}}{u_{1u}} \xi_a(u_{1u}, \beta_{1u}) \quad \frac{cm^3}{s} \qquad (6)$$

Z_{eff} = effective charge/atomic number = 1 (for Ar^+ ion)

c_{1u} = a constant $\cong 1$

f_{lu} = Absorption oscillator strength for the transition l $\rightarrow$ u[22,23]

$u_a = 13.6\, k_B T_e$ (eV)

$u_{1u} = (E_1 - E_u)/k_B T_e$

β_{1u} = a constant = $1 + [(Z_{eff}-1)/(Z_{eff}+1)] = 1$

[20] H. W. Drawin, "Collision and Transport Cross Sections," Report EUR-CEA-FC-383, Association Euratom C.E.A., Fontenay-aux-Roses, France (1967). [21] R. D. Taylor, and A. W. Ali, J. Appl. Phys. 64, 89 (1988); [22] C. H. Corliss and J. B. Shumaker, Jr., J. Res. Natl. Bur. Stand. (U.S.), Sect. A 71, 575–581 (1967); [23] J. Phys. B: At. Mol. Opt. Phys. 39, 2145 (2006).

Determination of deviation of plasma from LTE

- The function $\xi_a(u_{1u},\beta_{1u})$ can be determined[21] as

$$\xi_a\left(u_{1u},\beta_{1u}\right)=\frac{e^{-u_{1u}}}{1+u_{1u}}\cdot\left(\frac{1}{20+u_{1u}}+\ln\left\{1.25\times(1+\frac{1}{u_{1u}})\right\}\right) \qquad (7)$$

- Using equations (6) and (7) we can further define the magnitude for rate coefficient $k_{1u}(p_u)$ by electron-impact by a convenient and simpler expression with a functional dependence on T_e

$$k_{1u}(p_u)=d_{1u}\left(p_u\right)\cdot e^{-E_{1u}/k_BT_e} \qquad \frac{cm^3}{s} \qquad (8)$$

- Where the parameter $d_{1u}(p_u)$ is given by

$$d_{1u}(p_u)=E_{1u}{}^{y}\cdot p_u{}^{z} \qquad (9)$$

Where the exponent y and z can be determined from the fitting of the curves using Eqn. (8) and (9).

- Substituting the value of $k_{1u}(p_u)$ from Eqn. (4) in Eq (8) we can get

$$\ln\left\{\frac{N_u(p_u)\sum_{u\rangle l}A_{ul}}{n_eN_1}\right\}=\ln\left\{d_{1u}\left(p_u\right)\right\}-\frac{E_{1u}}{k_BT_e} \qquad (10)$$

- Substituting Eqn. (5) in Eqn. (10) we get

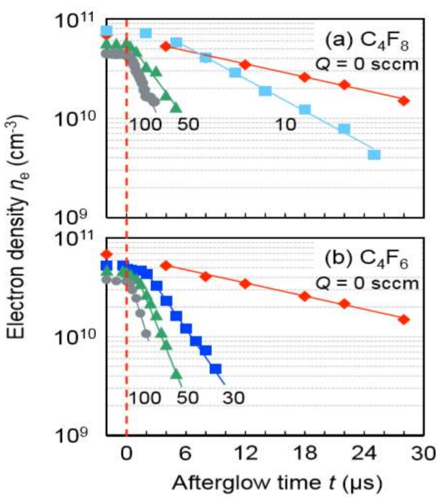
Determination of T_e

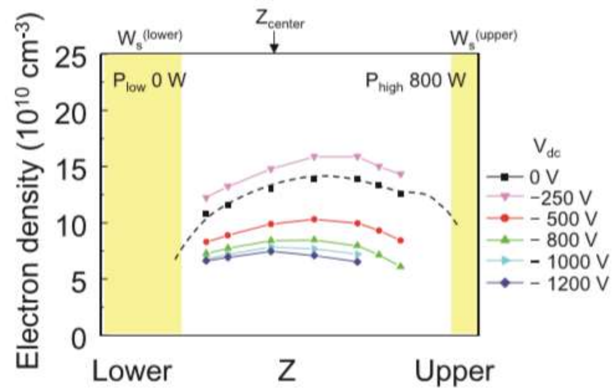
$$\frac{E_{1u}}{k_B T_e} = ln\left\{\frac{A_{ul} d_{1u}(p_u)}{\lambda_{ul} I_{ul} \sum_{u \rangle l} A_{ul}}\right\} + C_2 \qquad \textbf{(11)}$$

$$C_2 = \ln\left\{\frac{4 \cdot \pi}{h\, c\, n_e N_1 L_{pl}}\right\}$$ is a constant

- **Equations (11) represents the equation of a straight line, and the slope of the line will give the direct value of T_e in non-equilibrium plasmas satisfying the corona balance condition. We need to validate the the corona balance formalism.**

- **For this, we recall our earlier studies of plasma density measurement by surface wave probe**





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Rapid electron density decay observed by surface-wave probe in afterglow of pulsed fluorocarbon-based plasma

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To elucidate the pulsed fluorocarbon plasma behavior, a surface-wave probe with high time resolution was used to measure the electron density n_e in the afterglow of plasma. In a dual-frequency capacitively coupled plasma of fluorocarbon chemistry, e.g., an O_2-based C_4F_6 and Ar mixture, n_e vanished rapidly in a short time (~5 μs), whilst the dc current flowing onto the top electrode biased at −300 V decreased very slowly (decay time ~70 μs). This observation is clear evidence of ion–ion plasma formation by electron attachment in the afterglow. We point out that the electron attachment rates for fluorocarbon radicals significantly affect the electrons and ion–ion plasma behaviors observed at the afterglow phase.

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J. Phys. D: Appl. Phys. **50** (2017) 155201 (13pp) https://doi.org/10.1088/1361-6463/aa60f7

Spatial profiles of interelectrode electron density in direct current superposed dual-frequency capacitively coupled plasmas

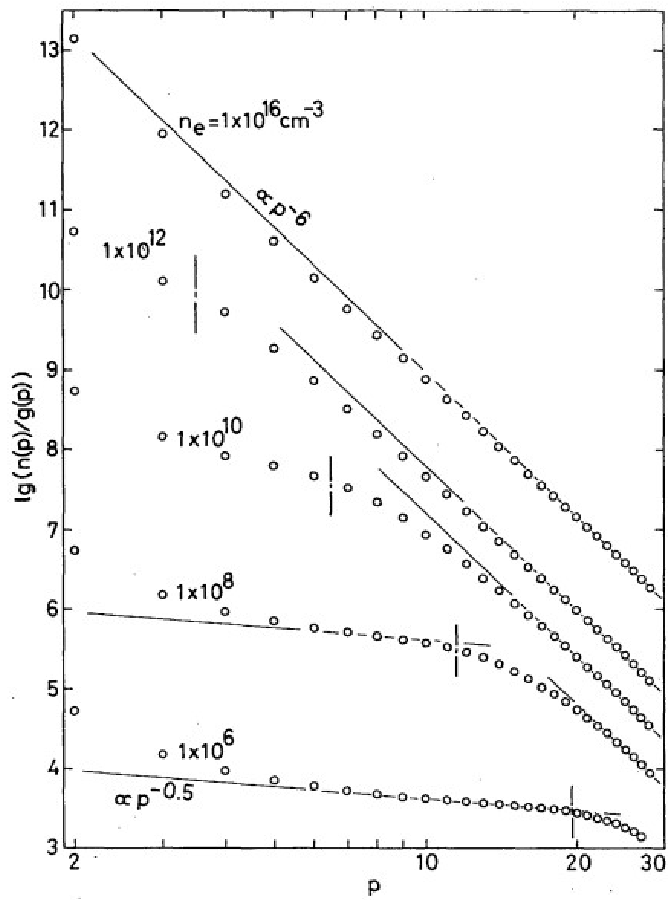
Yoshinobu Ohya[1,2], Kenji Ishikawa[1], Tatsuya Komuro[1], Tsuyoshi Yamaguchi[1], Keigo Takeda[1], Hiroki Kondo[1], Makoto Sekine[1] and Masaru Hori[1]

Validity of corona balance

- To validate the the corona balance formalism, we need to varify that, since the plasma is optically thin (low to moderate density ~ 10^9 to 10^{11} cm^{-3}), the relative population densities of the energy levels u of Ar (species we used for the present diagnosis) follow the expression[15]

$$\frac{N_u(p_u)}{g_u(p_u)} \alpha \; p_u^{-a} \qquad (12)$$

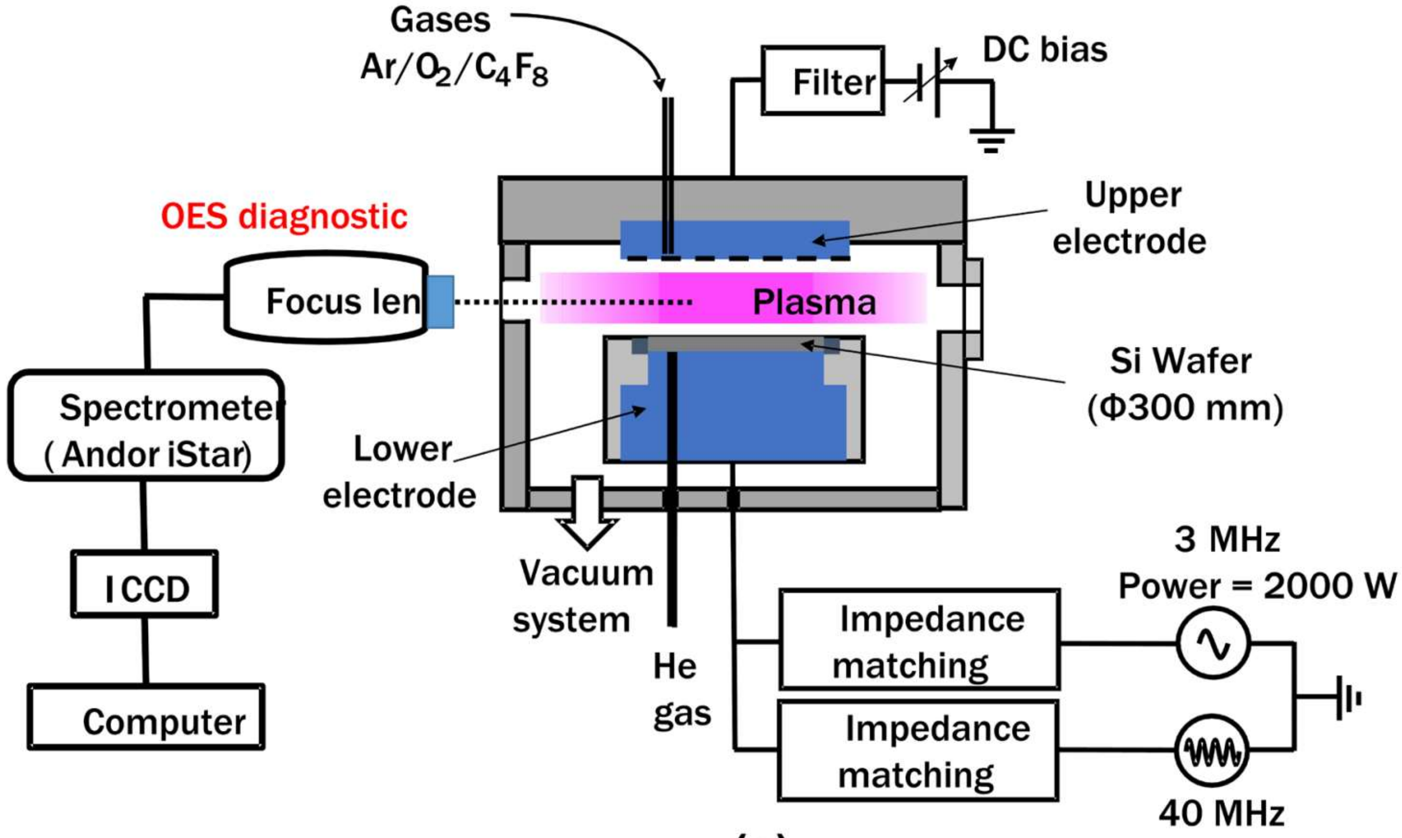
- When a = 0.5 → n_e ~ 10^6 cm^{-3}
- The corona balance extends to levels with p_u values up to approximately 20. [15]
- As the exponent increase from a = 0.5 to a = 3 the n_e increases from ~ 10^6 cm^{-3} to 10^{10} cm^{-3}
- For this case, the corona balance is only probable in excited states with values of p_u up to7.
- Also, there can be n_e ~ 10^{11} cm^{-3} with corona balance value for p_u between 2 and to 4 (relevant to our case) for a ≤ 6.



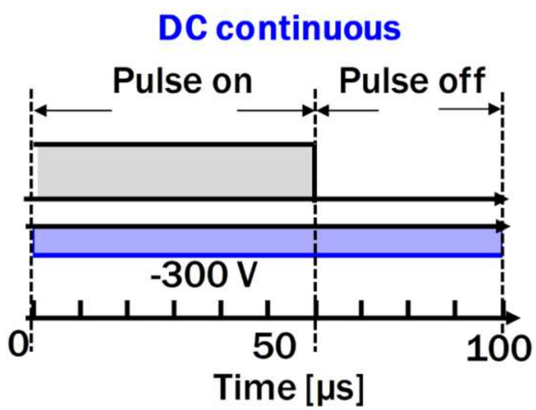
J. Phys. Soc. Japan 47, 273 (1979).

Experimental parameters

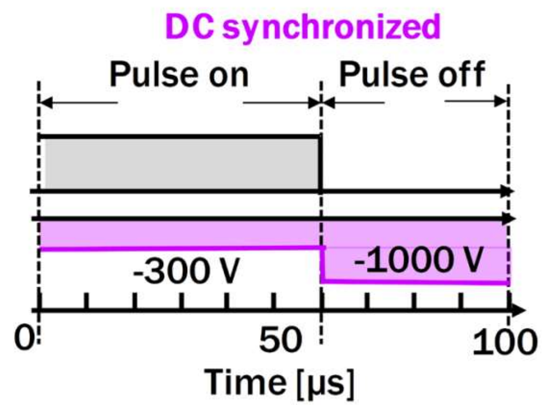
Experimental setups and operation parameters



(a)



(b)

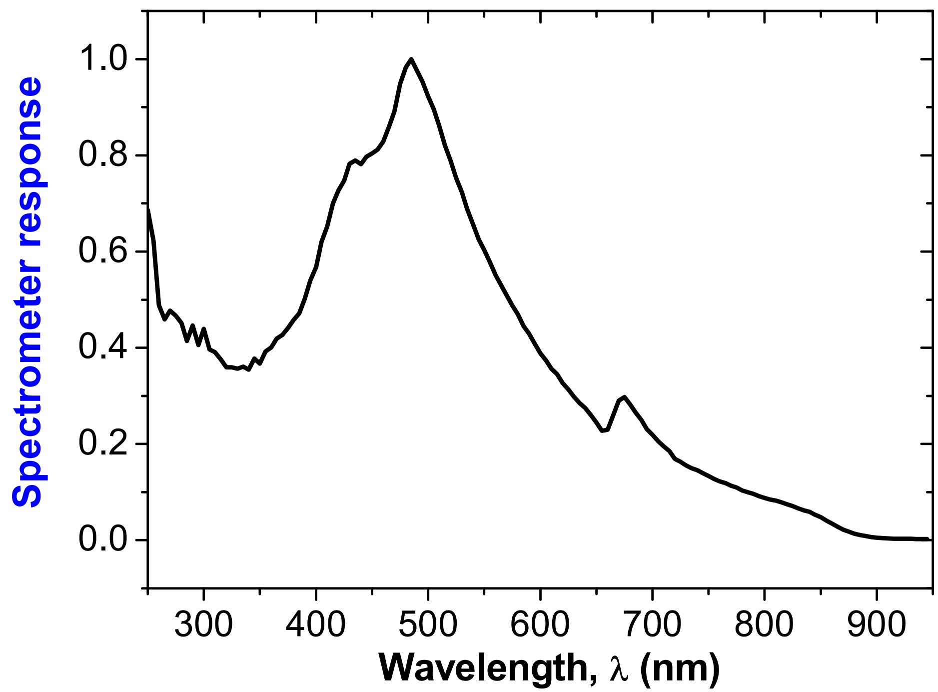


(c)

Conditions

Gas: C_4F_8 / Ar / O_2
= 60 / 300 / 30 sccm
Pressure: 2 Pa
RF power: 40 / 3 MHz
= 1000 / 2000 W
Pulse frequency: 10 kHz
Duty ratio: 60%
DC bias: -300 V (RF-on)
-1000 V (RF-off)

Sensitivity of Spectrometer: Response curve



Grating-2: Andor 1200-300
Optical Fiber: 1

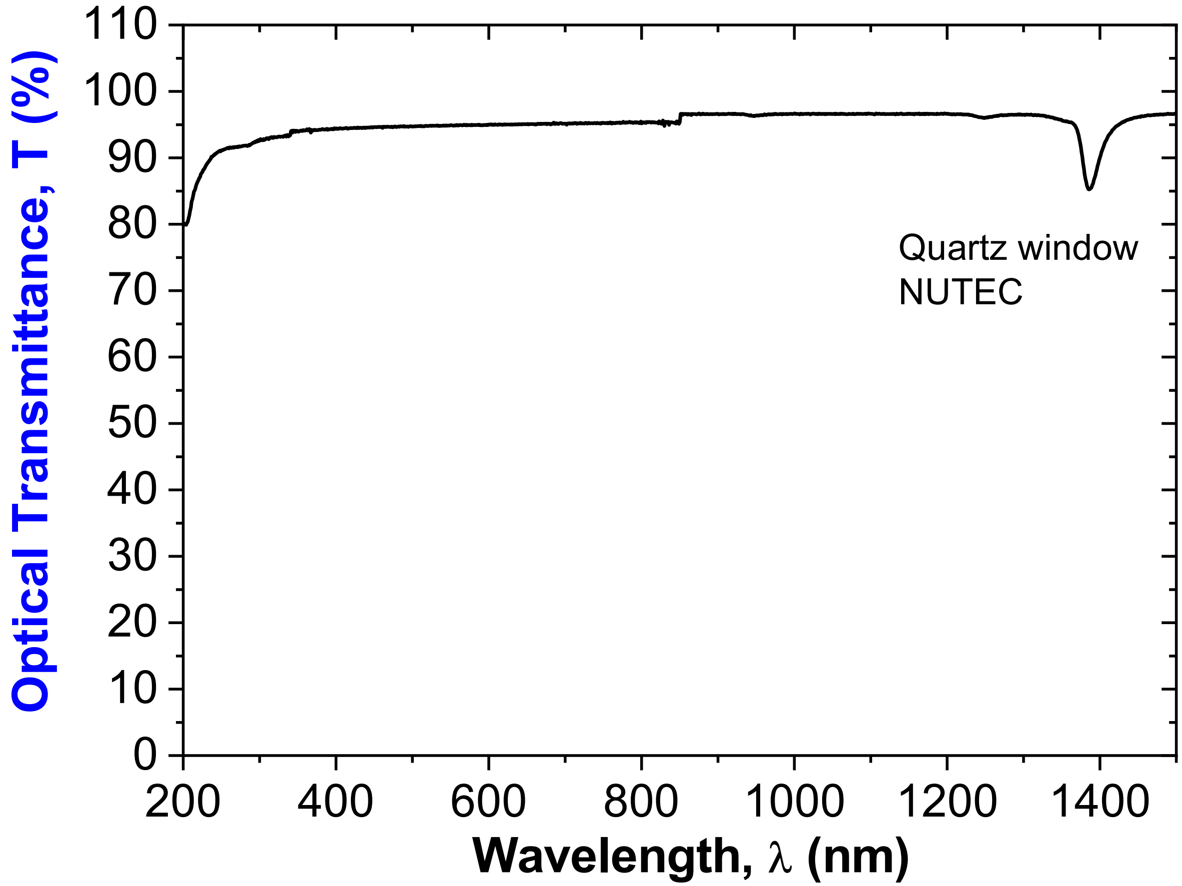
curves corresponding to the spectral response of the fiber + Grating + ICCD chain

Actual line intensity $I_a = I/f$
I = Measured spectral line intensity
F = Spectrometer response

$$\ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) = \frac{E_u}{k_B T_{ex}} + C_1$$

In our case, the correction term is accommodated in constant C_1.

Optical transmittance of the Quartz window of the system



The window can accommodate broad range of wavelengths for the OES

Computations of electron impact excitation rate coefficients

- Comparison with our data with existing literature of JAP paper
- Computation of parameters y and z

Table I: Spectroscopic parameters

λ_{ul} (nm)	E_u (eV)	g_u	A_{ul} (10^7 s^{-1})	Transition levels $E_u \rightarrow E_l$	p_u	f_{lu}
419.83	14.58	1	0.257	$5p[1/2]_0 \rightarrow 4s[3/2]_1^0$	3.395	2.26×10^{-3}
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706.87	14.84	5	0.20	$6s[3/2]_1^0 \rightarrow 4p[5/2]_2$	3.845	1.35×10^{-2}
726.52	14.86	3	0.017	$4d[3/2]_1^0 \rightarrow 4p[3/2]_1$	3.887	4.99×10^{-2}
731.67	15.02	3	0.096	$6s'[1/2]_1^0 \rightarrow 4p'[1/2]_1$	4.287	3.37×10^{-2}
750.39	13.48	1	4.450	$4p'[1/2]_0 \rightarrow 4s'[1/2]_1^0$	2.442	1.25×10^{-1}
751.47	13.27	1	4.020	$4p[1/2]_0 \rightarrow 4s[3/2]_1^0$	2.337	1.14×10^{-1}
763.51	13.17	5	2.452	$4p[3/2]_2 \rightarrow 4s[3/2]_2^0$	2.291	2.14×10^{-1}
772.42	13.33	3	1.170	$4p'[1/2]_1 \rightarrow 4s'[1/2]_0^0$	2.366	3.14×10^{-1}
811.53	13.08	7	3.310	$4p[5/2]_3 \rightarrow 4s[3/2]_2^0$	2.253	4.58×10^{-1}

Table II: Possible radiative transitions for emitted lines

λ_{ul} (nm)	Possible radiative Transitions $E_u \rightarrow E_l$ (u>l)	No of radiative transitions	$\sum_{u\rangle l} A_{ul}$ (10^7 s^{-1})	*y*	*z*
419.83	$5p[1/2]_0 \rightarrow 4s[3/2]_1^0$, $5p[1/2]_0 \rightarrow 4s'[1/2]_1^0$	2	0.375	-8.305	-2.624
425.12	$5p[1/2]_1 \rightarrow 4s[3/2]_2^0$, $5p[1/2]_1 \rightarrow 4s[1/2]_0^0$, $5p[1/2]_1 \rightarrow 4s'[1/2]_0^0$, $5p[1/2]_1 \rightarrow 4s'[1/2]_1^0$	4	0.08488	-9.445	-2.53
427.22	$5p[3/2]_1 \rightarrow 4s[3/2]_1^0$, $5p[3/2]_1 \rightarrow 4s'[1/2]_1^0$, $5p[3/2]_1 \rightarrow 4s[3/2]_2^0$, $5p[3/2]_1 \rightarrow 4s'[1/2]_0^0$	4	0.11797	-7.575	-4.487
434.52	$5p'[3/2]_1 \rightarrow 4s'[1/2]_1^0$, $5p'[3/2]_1 \rightarrow 4s[3/2]_1^0$, $5p'[3/2]_1 \rightarrow 4s[3/2]_2^0$, $5p'[3/2]_1 \rightarrow 4s'[1/2]_0^0$	4	0.0324	-6.575	-6.921
706.87	$6s[3/2]_1^0 \rightarrow 4p[5/2]_2$, $6s[3/2]_1^0 \rightarrow 4p[1/2]_1$, $6s[3/2]_1^0 \rightarrow 4p[3/2]_1$, $6s[3/2]_1^0 \rightarrow 4p[3/2]_2$, $6s[3/2]_1^0 \rightarrow 4p[1/2]_0$	5	0.5191	-6.30	-4.621
726.52	$4d[3/2]_1^0 \rightarrow 4p[3/2]_1$, $4d[3/2]_1^0 \rightarrow 4p[1/2]_0$, $4d[3/2]_1^0 \rightarrow 4p'[3/2]_1$ $4d[3/2]_1^0 \rightarrow 4p'[1/2]_1$	4	0.0173	-6.275	-3.617
731.67	$6s'[1/2]_1^0 \rightarrow 4p'[1/2]_1$, $6s'[1/2]_1^0 \rightarrow 4p'[1/2]_0$, $6s'[1/2]_1^0 \rightarrow 4p'[3/2]_2$, $6s'[1/2]_1^0 \rightarrow 4p'[3/2]_1$, $6s'[1/2]_1^0 \rightarrow 4p[3/2]_2$, $6s'[1/2]_1^0 \rightarrow 4p[5/2]_2$	6	0.4559	-3.987	-7.605
750.39	$4p'[1/2]_0 \rightarrow 4s'[1/2]_1^0$, $4p'[1/2]_0 \rightarrow 4s[3/2]_1^0$	2	4.4736	-6.95	-5.735
751.47	$4p[1/2]_0 \rightarrow 4s[3/2]_1^0$, $4p[1/2]_0 \rightarrow 4s'[1/2]_1^0$	2	4.104	-9.991	2.725
763.51	$4p[3/2]_2 \rightarrow 4s[3/2]_2^0$, $4p[3/2]_2 \rightarrow 4s[3/2]_1^0$, $4p[1/2]_2 \rightarrow 4s'[1/2]_1^0$	3	3.443	-10.937	6.245
772.42	$4p'[1/2]_1 \rightarrow 4s'[1/2]_0^0$, $4p'[1/2]_1 \rightarrow 4s'[1/2]_1^0$, $4p'[1/2]_1 \rightarrow 4s[3/2]_1^0$, $4p'[1/2]_1 \rightarrow 4s[3/2]_2^0$	4	3.522	-14.994	18.992
811.53	$4p[5/2]_3 \rightarrow 4s[3/2]_2^0$	1	3.310	-7.092	-4.928

Rate coefficient and fitting parameters y and z

Comparison of rate coefficients with the literature

Taylor and Ali: JAP 64,89 (1988)

$$X(i,j) = \frac{4.3\times 10^{-6} f(j,i)\exp[-E(j,i)/T_e]}{E(j,i)T_e^{1/2}}\Psi(j,i), \tag{11}$$

where $E(j,i) = E(j) - E(i), i<j, f(j,i)$ is the oscillator strength, and T_e is the electron temperature in units of eV. An effective Gaunt factor of 0.2 is used for ions,[23,24] while for neutrals

$$\Psi(j,i) = \left(1.0 + \frac{E(j,i)}{T_e}\right)^{-1}\left\{\left(20.0 + \frac{E(j,i)}{T_e}\right)^{-1} + \ln\left[1.25\left(1.0 + \frac{T_e}{E(j,i)}\right)\right]\right\}. \tag{12}$$

There is a typing error in Eqn 11 of the paper. The power of T_e in denominator will be 3/2

Our case

$$k_{1u}(p_u) = 8.68\times 10^{-8} c_{1u} Z_{eff}^{-3} f_{1u} \times \frac{u_a^{3/2}}{u_{1u}} \xi_a(u_{1u};\beta_{1u}) \quad \frac{cm^3}{s} \tag{6}$$

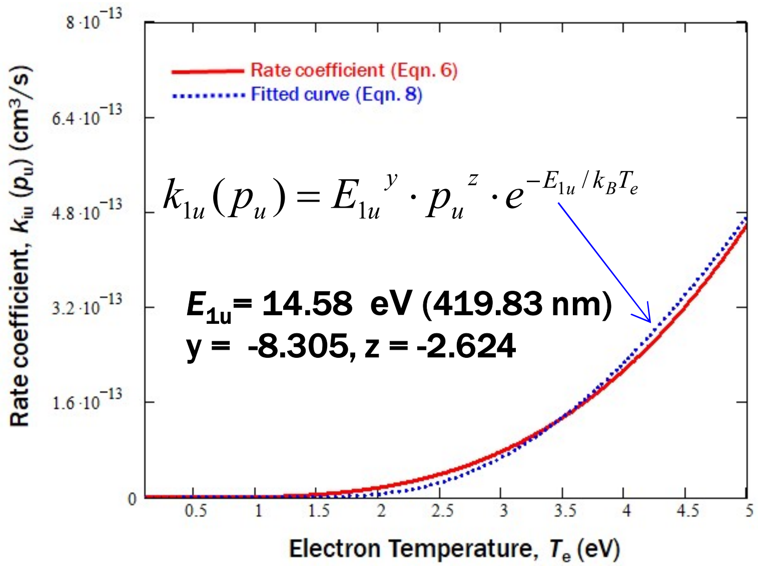
where the term Z_{eff} corresponds to the effective charge/atomic number (= 1 for Ar^+ ion), c_{1u} represents a constant (≅ 1), and f_{1u} represents the absorption oscillator strength.[54] The other terms are $u_a = 13.6\ k_B T_e$ (eV), $u_{1u} = (E_1 - E_u)/k_B T_e$, and $\beta_{1u} = 1 + [(Z_{eff}-1)/(Z_{eff}+1)]$. The function $\xi_a(u_{1u}, \beta_{1u})$ can be determined[53] as

$$\xi_a(u_{1u};\beta_{1u}) = \frac{e^{-u_{1u}}}{1+u_{1u}}\cdot\left(\frac{1}{20+u_{1u}} + \ln\left\{1.25\times(1+\frac{1}{u_{1u}})\right\}\right) \tag{7}$$

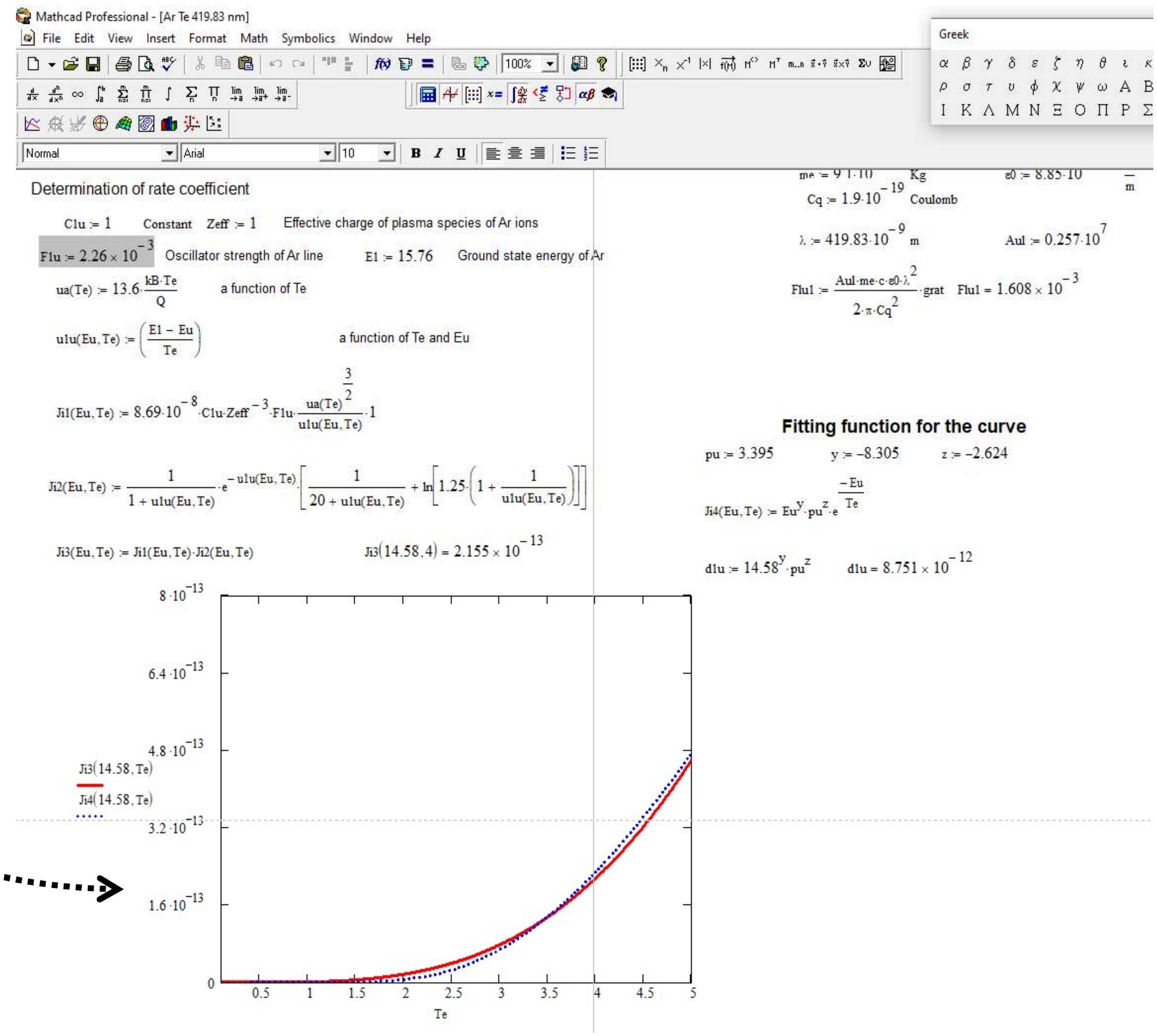
We can further define the magnitude for rate coefficient $k_{1u}(p_u)$ by electron-impact by a convenient and simpler expression with functional dependence on T_e using equations (6) and (7) as follows:

$$k_{1u}(p_u) = d_{1u}(p_u)\cdot e^{-E_{1u}/k_B T_e} \quad \frac{cm^3}{s} \tag{8}$$

Rate coefficients: to obtain fitting parameters



Computed in MathCAD platform



Rate coefficient for each transition was computed

Rate coefficient and fitting parameters y and z

Taylor and Ali: JAP 64,89 (1988)

$$X(i,j) = \frac{4.3\times 10^{-6} f(j,i)\exp[-E(j,i)/T_e]}{E(j,i)T_e^{1/2}}\Psi(j,i), \quad (11)$$

There is a typing error in Eqn 11.
The power of Te in denominator will be 3/2

Determination of rate coefficient

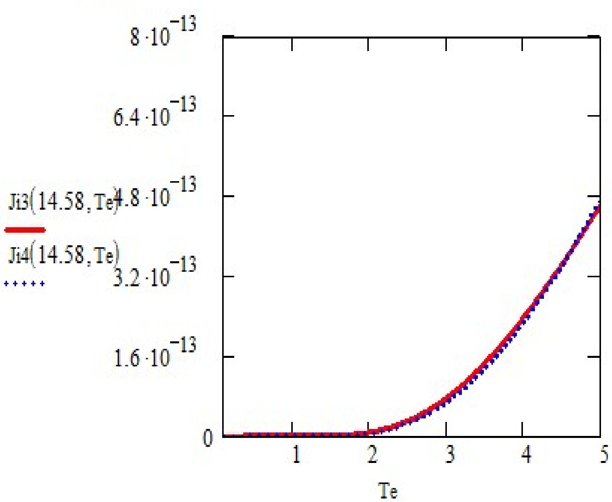
$C1u := 1$ Constant $Zeff := 1$ Effective charge of plasma species of Ar ions

$F1u := 2.26\times 10^{-3}$ Oscillator strength of Ar line $E1 := 15.76$ Ground state energy of Ar

Taylor & Ali: JAP

$$Si(Eu,Te) := \left(1+\frac{Eu}{Te}\right)^{-1}\cdot\left[\left(20+\frac{Eu}{Te}\right)^{-1} + \ln\left[1.25\cdot\left(1+\frac{Te}{Eu}\right)\right]\right]$$

$$Ji3(Eu,Te) := 4.3\cdot 10^{-6}\cdot\frac{F1u}{Eu\cdot Te^{\frac{3}{2}}}\cdot e^{\frac{-Eu}{Te}}\cdot Si(Eu,Te)$$



$\lambda := 419.83\cdot 10^{-9}$ m $\quad Aul := 0.257\cdot 10^{7}$

$$Flu1 := \frac{Aul\cdot me\cdot c\cdot \varepsilon 0\cdot \lambda^2}{2\cdot\pi\cdot Cq^2}\cdot grat \qquad Flu1 = 1.608\times 10^{-3}$$

Fitting function for the curve Ji4

$pu := 3.395 \qquad y := -8.305 \qquad z := -2.624$

$$Ji4(Eu,Te) := Eu^{y}\cdot pu^{z}\cdot e^{\frac{-Eu}{Te}}$$

$d1u := 14.58^{y}\cdot pu^{z} \qquad d1u = 8.751\times 10^{-12}$

Our case:

$ua(Te) := 13.6\cdot\frac{kB\cdot Te}{Q}$ a function of Te $\qquad u1u(Eu,Te) := \left(\frac{E1-Eu}{Te}\right)$ a function of Te and Eu

$$Ji1(Eu,Te) := 8.69\cdot 10^{-8}\cdot C1u\cdot Zeff^{-3}\cdot F1u\cdot\frac{ua(Te)^{\frac{3}{2}}}{u1u(Eu,Te)}\cdot 1$$

$$Ji2(Eu,Te) := \frac{1}{1+u1u(Eu,Te)}\cdot e^{-u1u(Eu,Te)}\left[\frac{1}{20+u1u(Eu,Te)} + \ln\left[1.25\cdot\left(1+\frac{1}{u1u(Eu,Te)}\right)\right]\right]$$

$Ji5(Eu,Te) := Ji1(Eu,Te)\cdot Ji2(Eu,Te) \qquad Ji5(14.58,4) = 2.155\times 10^{-13}$

Rate coefficient and fitting parameters y and z

Our case

$$k_{1u}(p_u) = 8.68\times10^{-8} c_{1u} Z_{eff}^{-3} f_{1u} \times \frac{u_a^{3/2}}{u_{1u}} \xi_a(u_{1u}, \beta_{1u}) \quad \frac{cm^3}{s} \qquad (6)$$

Our case:

$ua(Te) := 13.6\cdot\frac{kB\cdot Te}{Q}$ a function of Te

$u1u(Eu, Te) := \left(\frac{E1 - Eu}{Te}\right)$ a function of Te and Eu

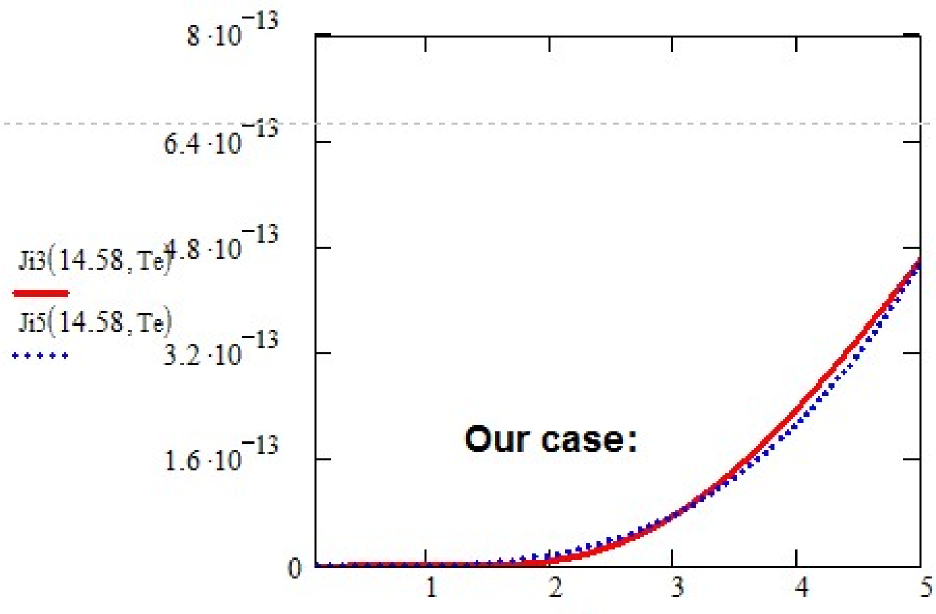
$$Ji1(Eu,Te) := 8.69\cdot10^{-8}\cdot C1u\cdot Zeff^{-3}\cdot F1u\cdot\frac{ua(Te)^{\frac{3}{2}}}{u1u(Eu,Te)}\cdot 1$$

$$Ji2(Eu,Te) := \frac{1}{1+u1u(Eu,Te)}\cdot e^{-u1u(Eu,Te)}\cdot\left[\frac{1}{20+u1u(Eu,Te)} + \ln\left[1.25\cdot\left(1+\frac{1}{u1u(Eu,Te)}\right)\right]\right]$$

$Ji5(Eu,Te) := Ji1(Eu,Te)\cdot Ji2(Eu,Te)$ $\qquad Ji5(14.58, 4) = 2.155\times10^{-13}$

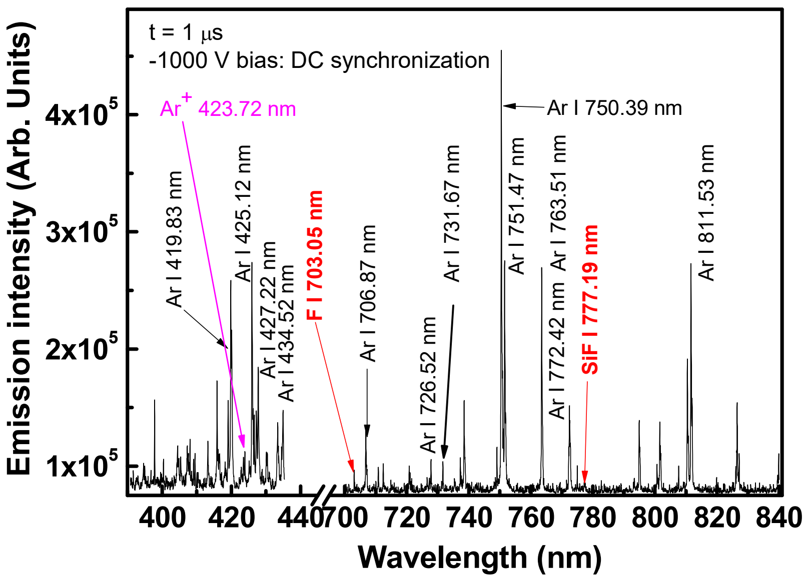
Our case J_{i5}

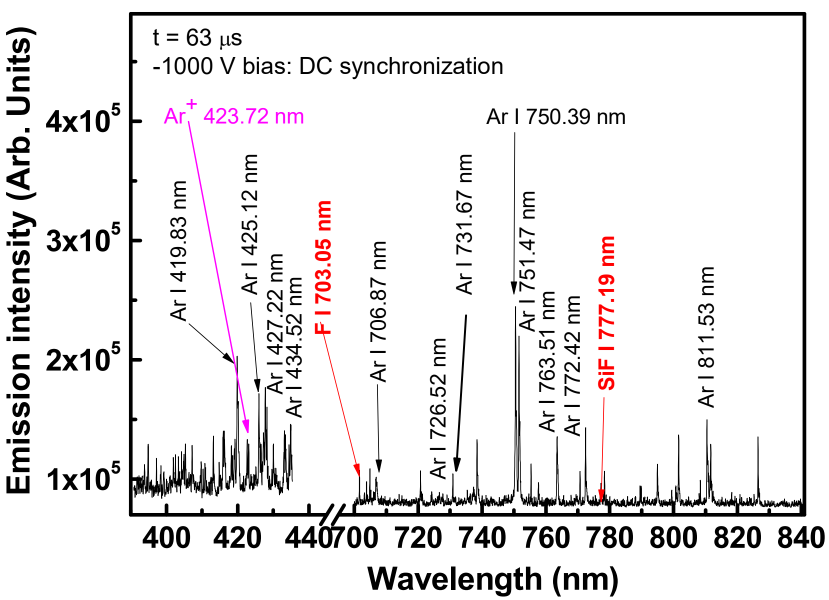
Taylor-Ali case J_{i3}



OES SPECTRUM: Examples in DC synchronized condition

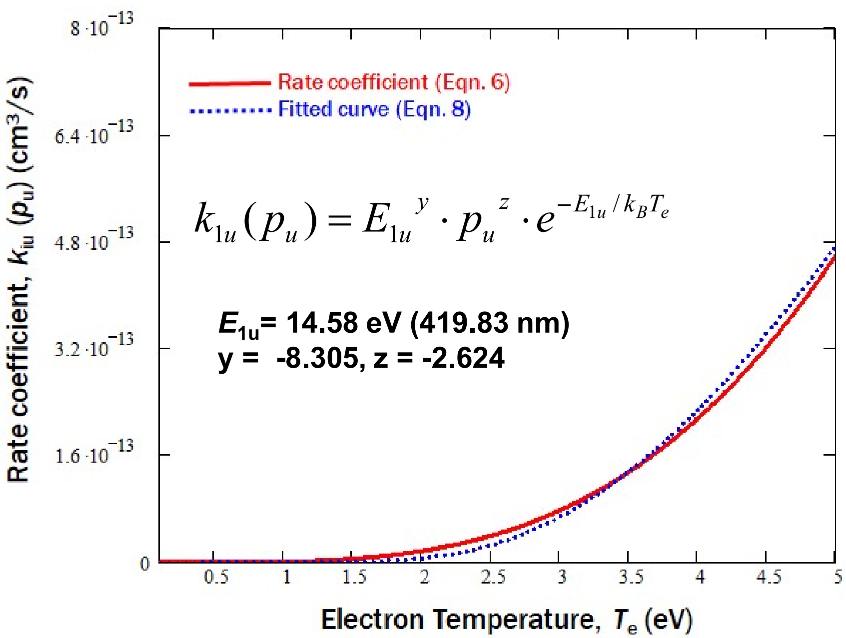
Typical OES spectra during glow (pulse on) at t = 1 μs and after glow (pulse off) at t = 63 μs

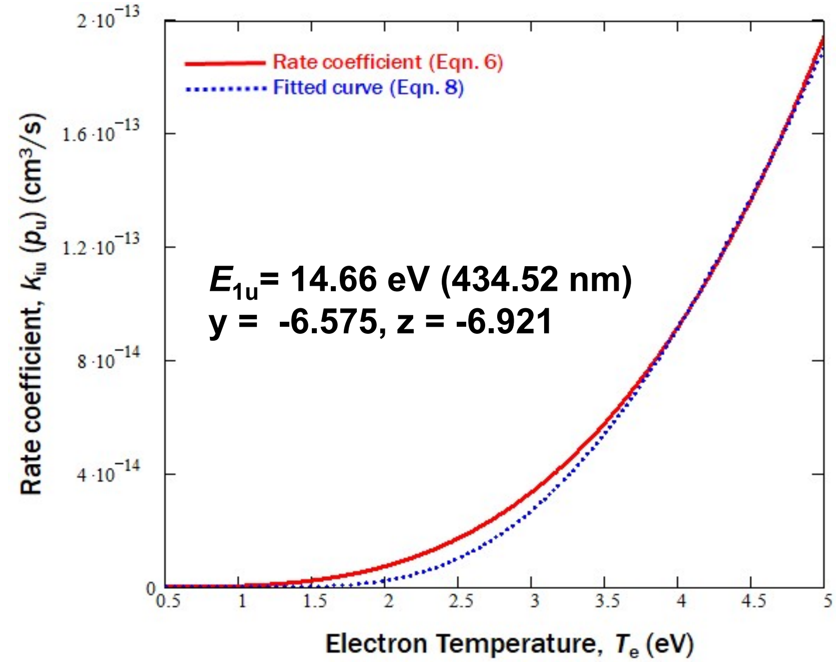


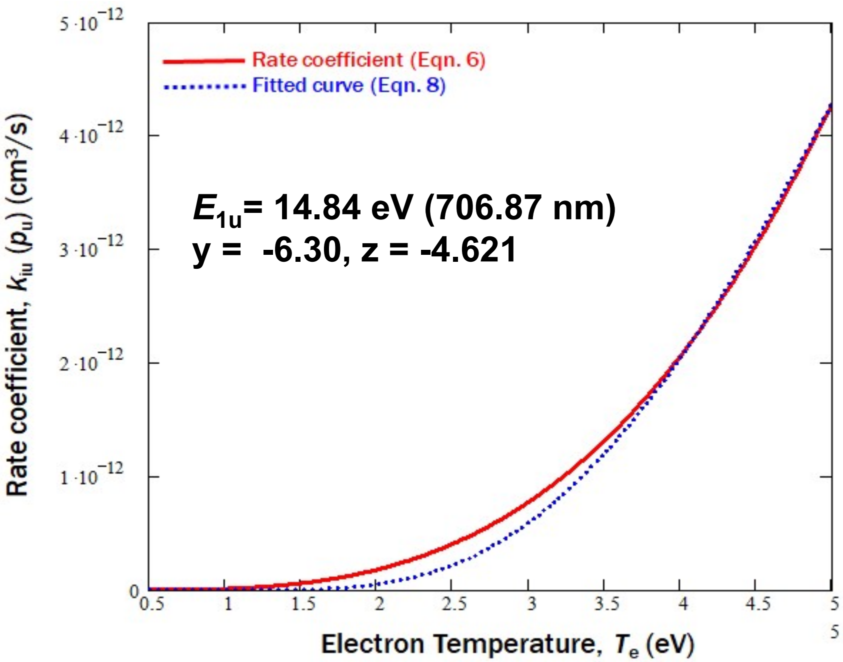


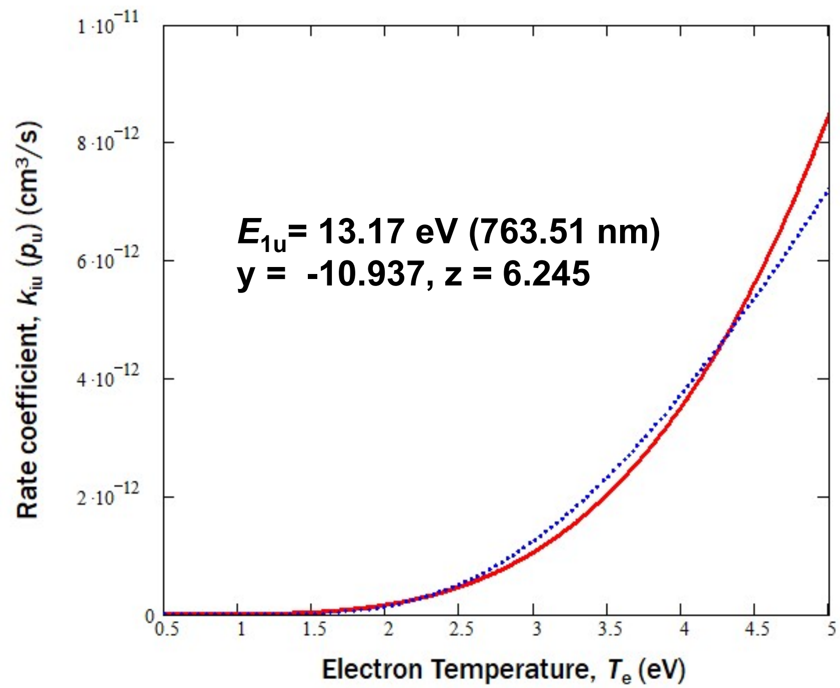
λ(Table I) Used for the calculation	λ (measured)	I(nm) At t = 1μs	I(nm) At t = 63μs
419.83	419.88041	238930	203036
425.12	425.14201	104705	108210
427.22	427.22953	146390	138939
434.52	434.53685	112450	102979
706.87	706.85925	123008	100958
726.52	726.50789	86898.1	84696.4
731.67	731.67283	103970	84518.8
750.39	750.39233	292102	151900
751.47	751.48544	224218	151487
763.51	763.50964	269491	131890
772.42	772.41849	150203	141566
811.53	811.52448	155569	95117

Rate coefficients: to obtain fitting parameters

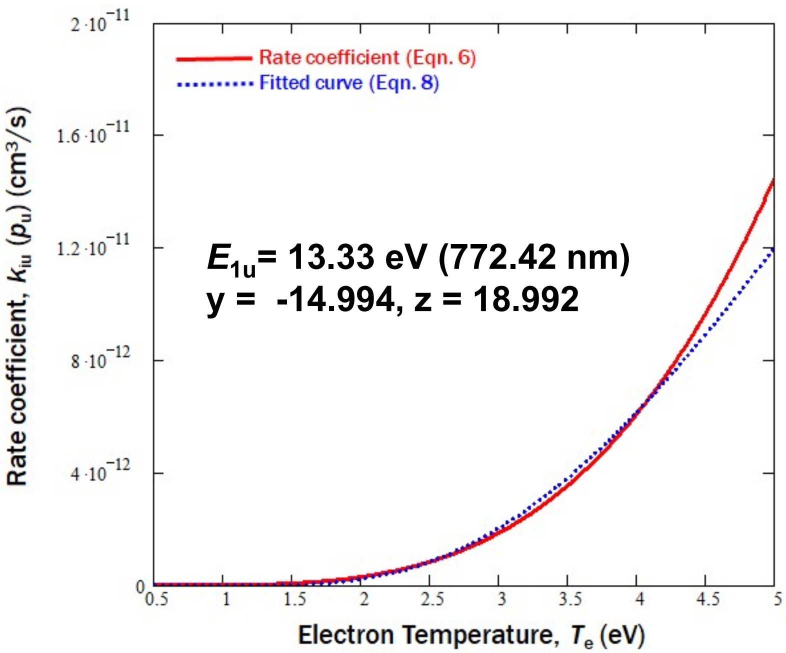


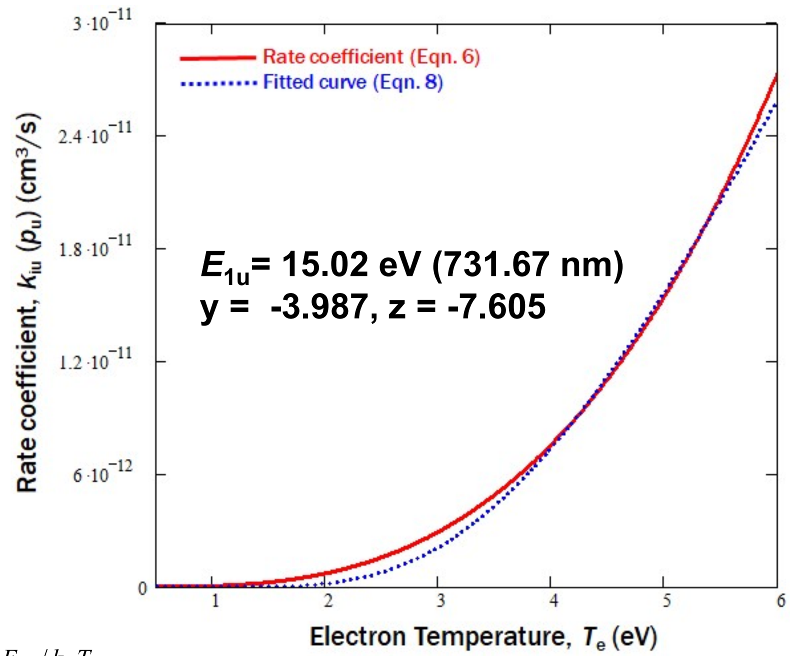




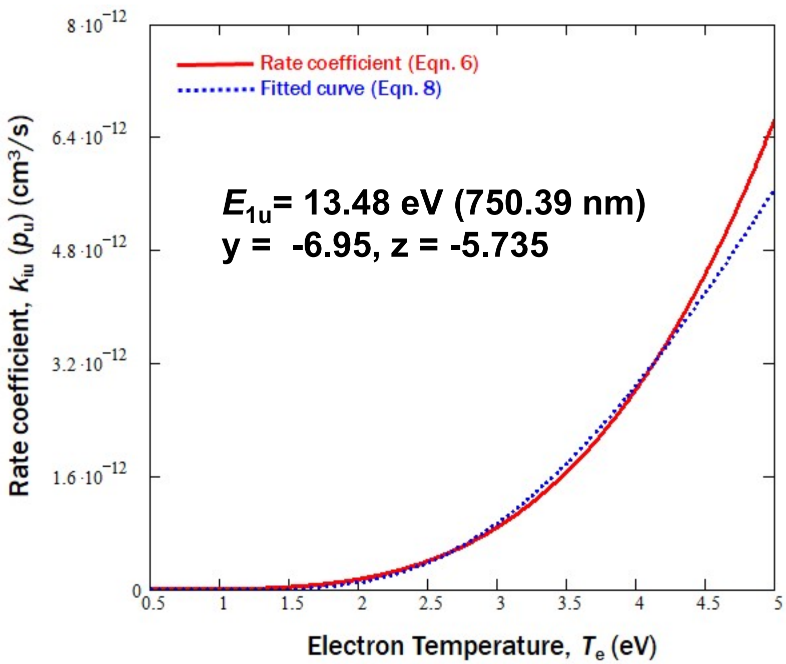


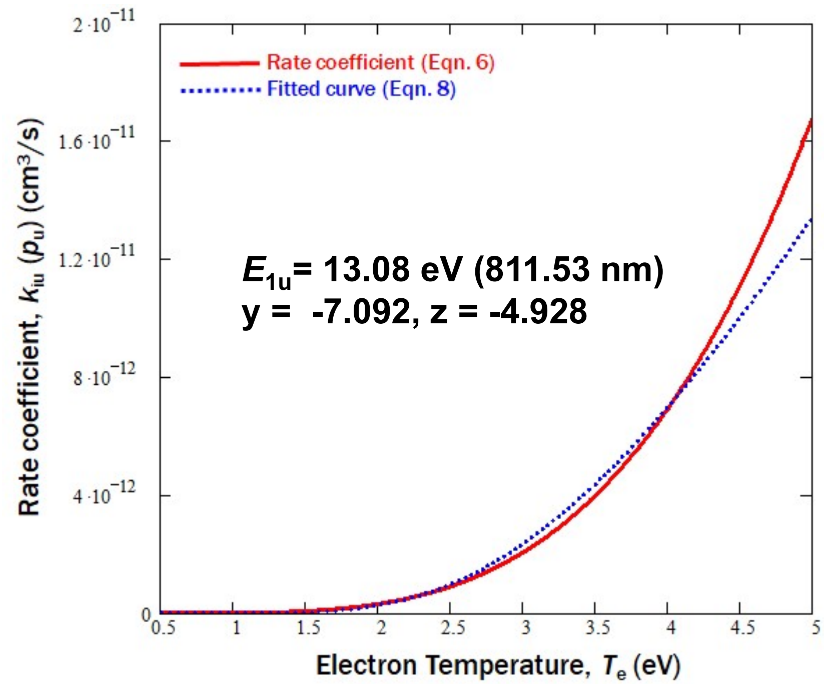
Rate coefficients: to obtain fitting parameters





$$k_{1u}(p_u) = E_{1u}{}^{y} \cdot p_u{}^{z} \cdot e^{-E_{1u}/k_B T_e}$$

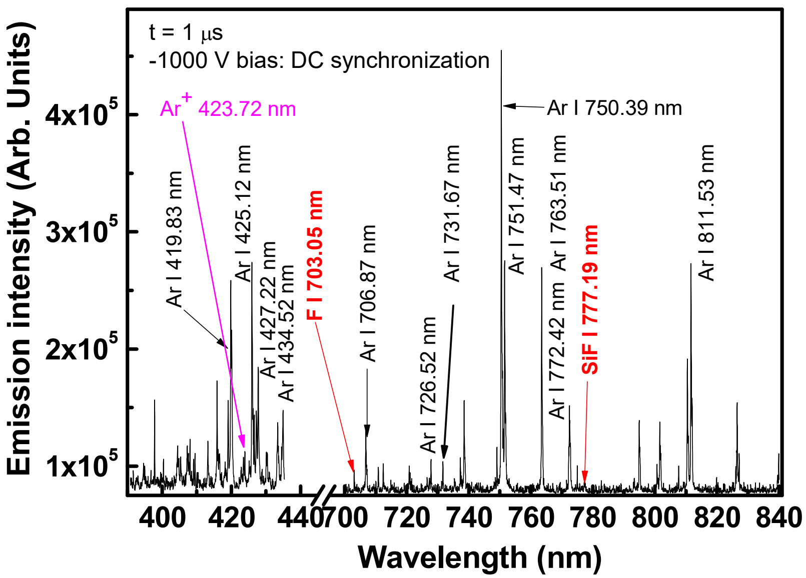


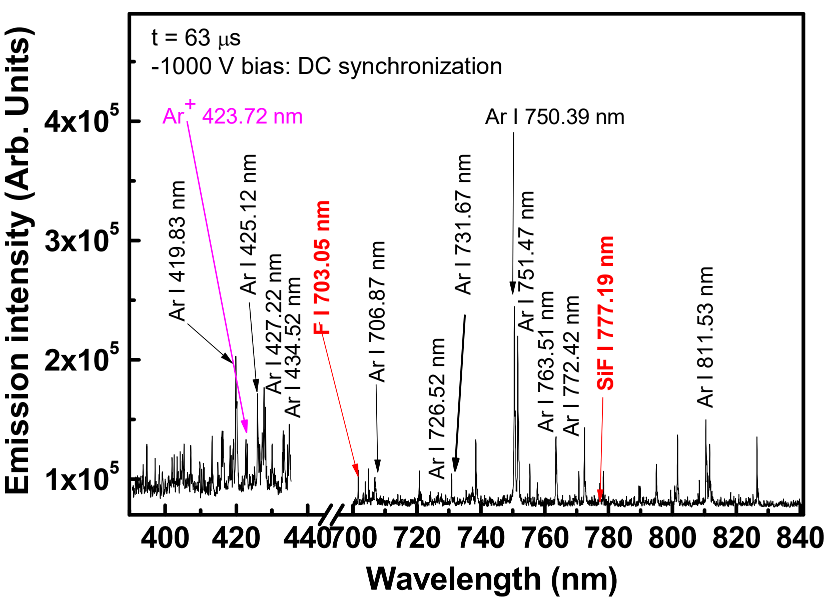


The parameter of corona model and validity of corona approximation

OES SPECTRUM: Examples in DC synchronized condition

Typical OES spectrum during glow (pulse on) at t = 1 μs and after glow (pulse off) at t = 63 μs





λ(Table I) Used for the calculation	λ (measured)	I(nm) At t = 1μs	I(nm) At t = 63μs
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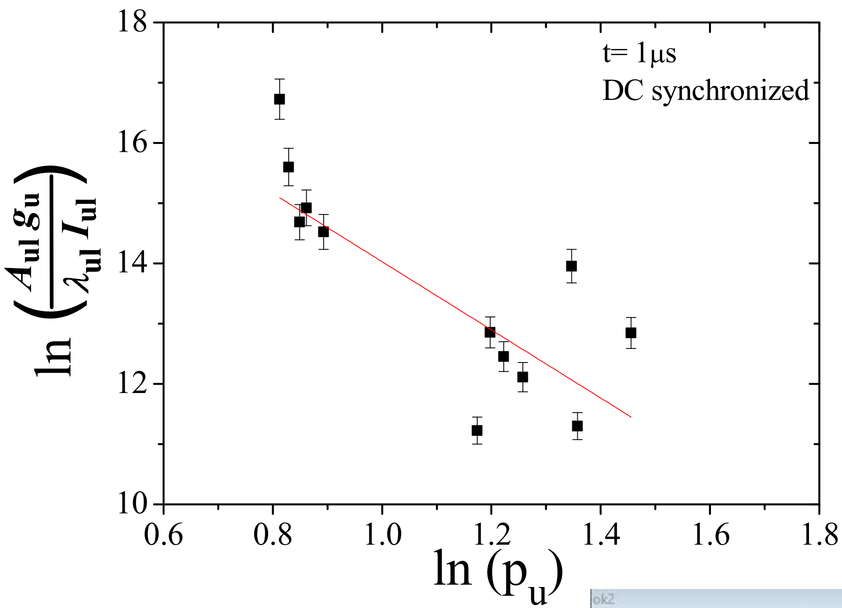
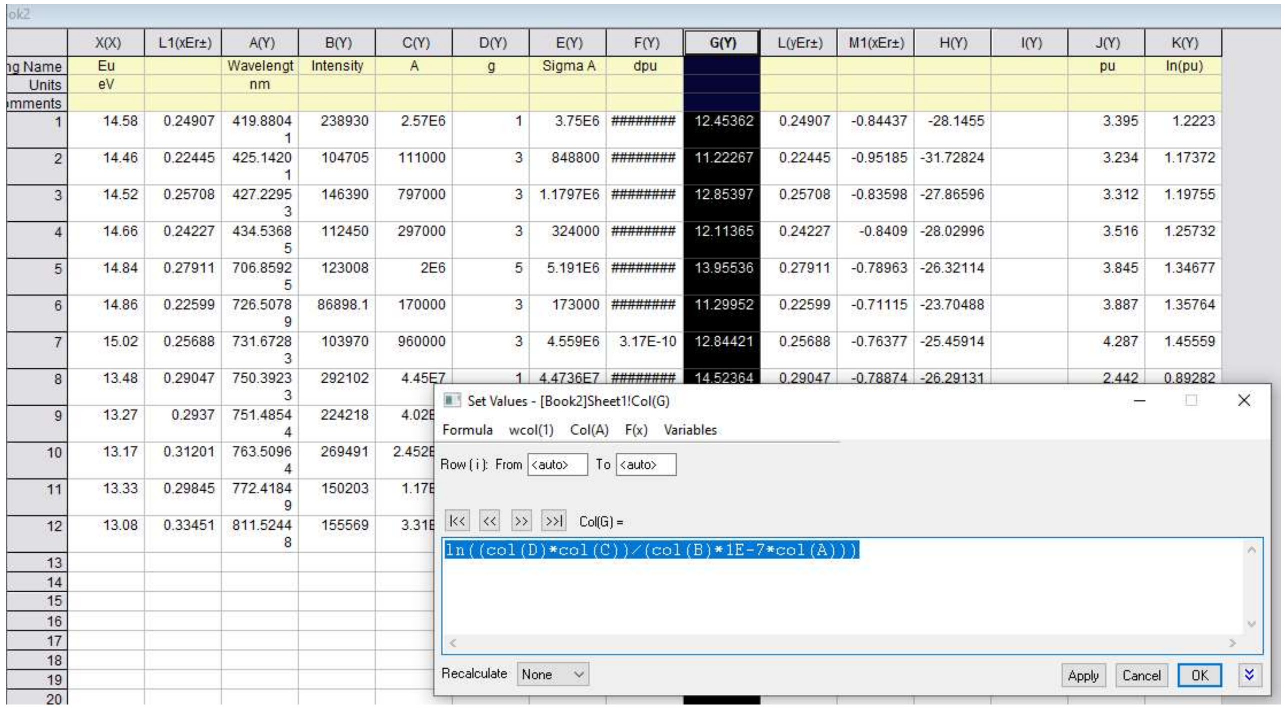
726.52	726.50789	86898.1	84696.4
731.67	731.67283	103970	84518.8
750.39	750.39233	292102	151900
751.47	751.48544	224218	151487
763.51	763.50964	269491	131890
772.42	772.41849	150203	141566
811.53	811.52448	155569	95117

Corona factor (a) of Eqn 12



$$\ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) = -5.6 \cdot \ln(p_u) + 19.6$$



	X(X)	L1(xEr±)	A(Y)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	L(yEr±)	M1(xEr±)	H(Y)	I(Y)	J(Y)	K(Y)
ng Name	Eu		Wavelengt	Intensity	A	g	Sigma A	dpu						pu	ln(pu)
Units	eV		nm												
mments															
1	14.58	0.24907	419.88041	238930	2.57E6	1	3.75E6	########	12.45362	0.24907	-0.84437	-28.1455		3.395	1.2223
2	14.46	0.22445	425.14201	104705	111000	3	848800	########	11.22267	0.22445	-0.95185	-31.72824		3.234	1.17372
3	14.52	0.25708	427.22953	146390	797000	3	1.1797E6	########	12.85397	0.25708	-0.83598	-27.86596		3.312	1.19755
4	14.66	0.24227	434.53685	112450	297000	3	324000	########	12.11365	0.24227	-0.8409	-28.02996		3.516	1.25732
5	14.84	0.27911	706.85925	123008	2E6	5	5.191E6	########	13.95536	0.27911	-0.78963	-26.32114		3.845	1.34677
6	14.86	0.22599	726.50789	86898.1	170000	3	173000	########	11.29952	0.22599	-0.71115	-23.70488		3.887	1.35764
7	15.02	0.25688	731.67283	103970	960000	3	4.559E6	3.17E-10	12.84421	0.25688	-0.76377	-25.45914		4.287	1.45559
8	13.48	0.29047	750.39233	292102	4.45E7	1	4.4736E7	########	14.52364	0.29047	-0.78874	-26.29131		2.442	0.89282
9	13.27	0.2937	751.48544	224218	4.02E										
10	13.17	0.31201	763.50964	269491	2.452E										
11	13.33	0.29845	772.41849	150203	1.17E										
12	13.08	0.33451	811.52448	155569	3.31E										
13															
14															
15															
16															
17															
18															
19															
20															

Set Values - [Book2]Sheet1!Col(G)

Formula wcol(1) Col(A) F(x) Variables

Row (i): From <auto> To <auto>

Col(G) =

```
ln((col(D)*col(C))/(col(B)*1E-7*col(A)))
```

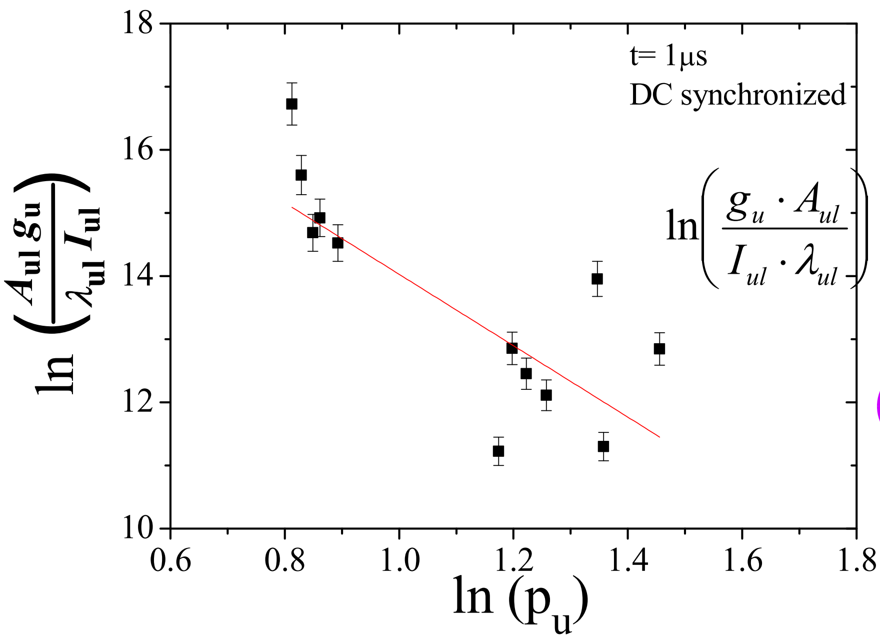
Recalculate None

Apply Cancel OK

Relative population densities as a function of their effective principal quantum number p_u

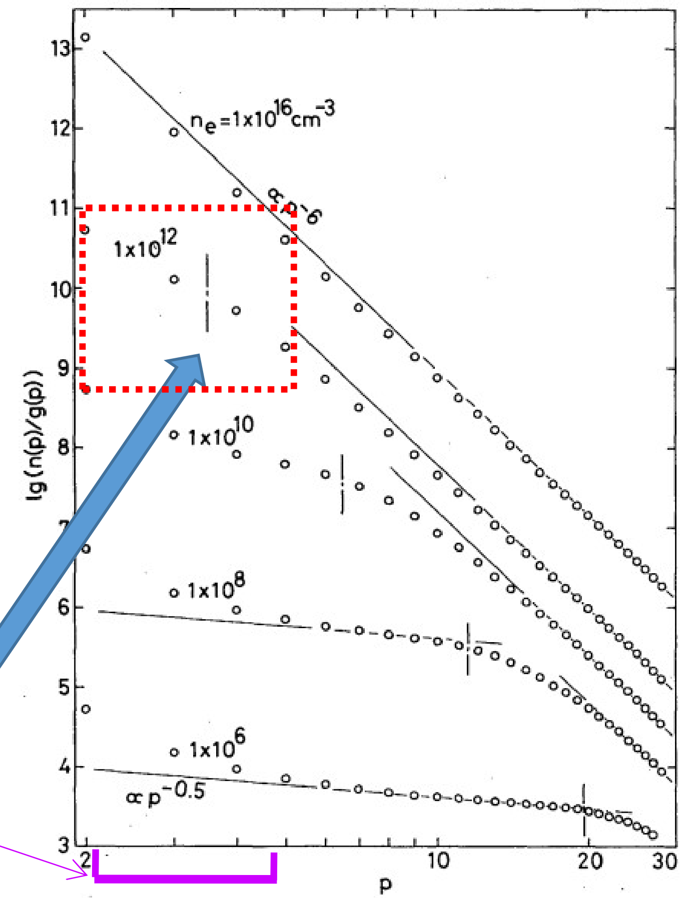
Verification of corona balance $\frac{N_u(p_u)}{g_u(p_u)} \alpha \; p_u^{-a}$

Corona balance formalism



$$\ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) = -5.6 \cdot \ln(p_u) + 19.6$$

$a \sim 5.6$



J. Phys. Soc. Japan 47, 273 (1979).

$2.253 \le p_u \le 4.287$ → Well within the corona balance

$4 \le a \le 6$

Our experiments

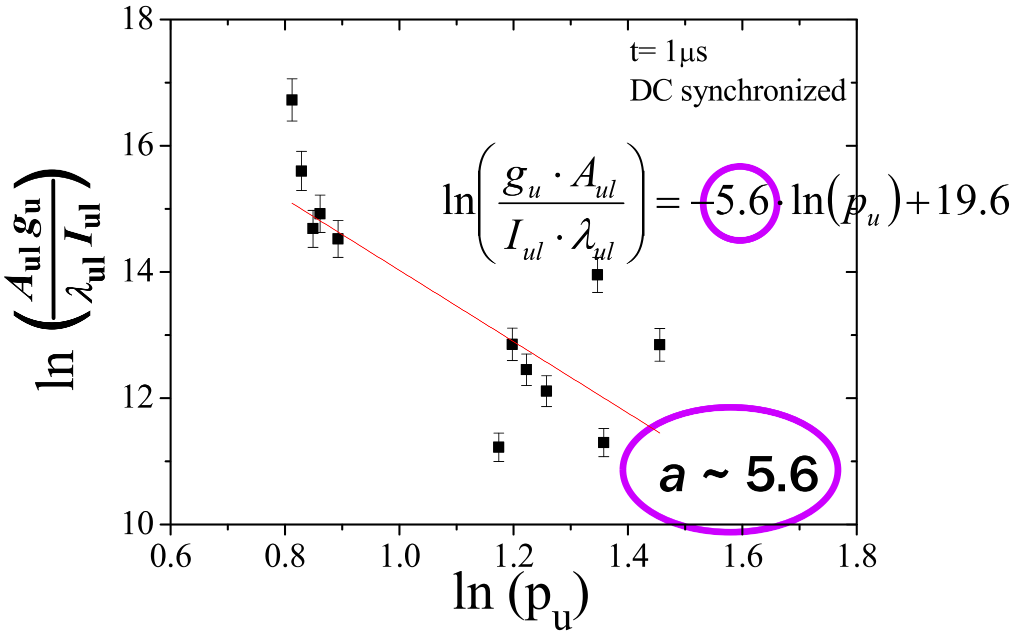
- The higher value of $a \sim 5.6$ in our experiment suggests that $n_e \sim 10^{11} \sim 10^{13}\ cm^{-3}$

Relative population densities as a function of their effective principal quantum number p_u

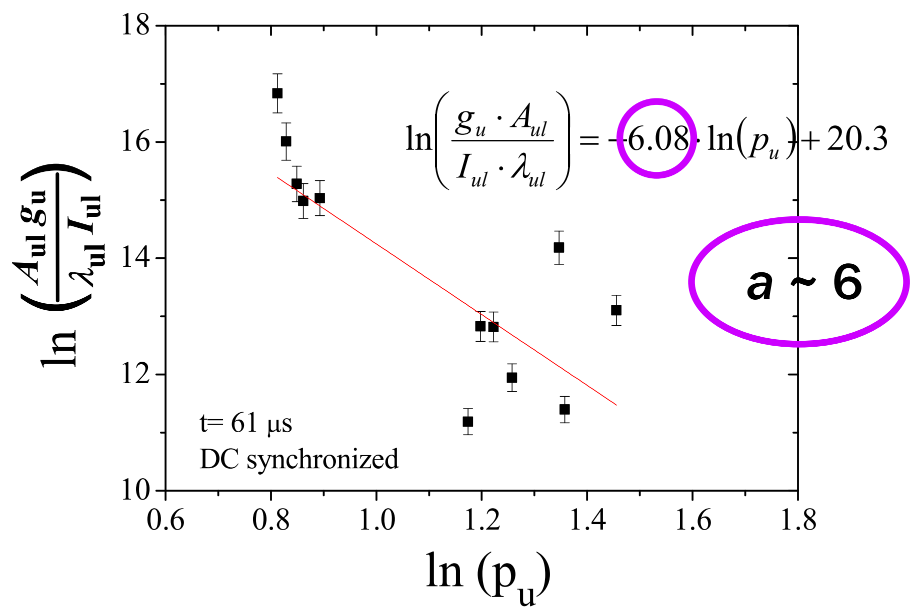
Verification of corona balance $\frac{N_u(p_u)}{g_u(p_u)} \alpha\ p_u^{-a}$

DC synchronous condition

t = 1 μs



t = 61 μs



2.253 $\leq p_u \leq$ 4.287 ➡ **Well within the corona balance**

Experimental results and discussion

1. Boltzmann Plot: Excitation temperature: T_{ex}

$$\ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) = \frac{E_u}{k_B T_{ex}} + C_1 \quad \Rightarrow E_u = k_B T_{ex} \cdot \ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) + \text{constant}$$

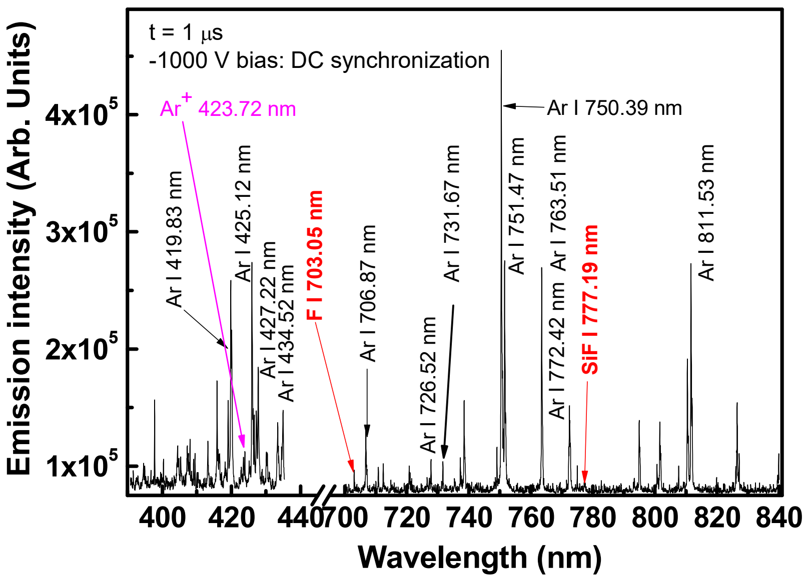
2. Modified Boltzmann equation: Electron temperature: T_e

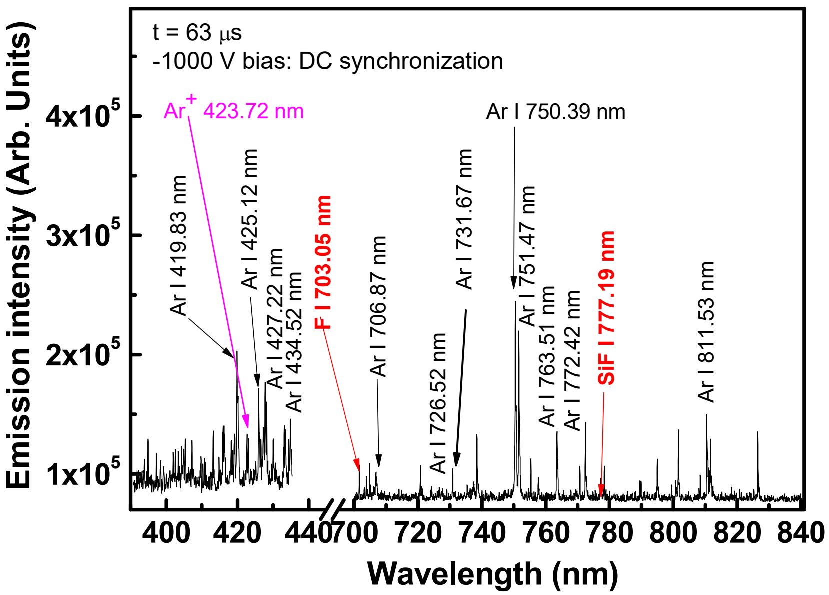
$$\ln\left\{\frac{A_{ul} d_{1u}(p_u)}{\lambda_{ul} I_{ul} \sum_{u\rangle l} A_{ul}}\right\} = \frac{E_{1u}}{k_B T_e} + \mathrm{C}_2 \quad \Rightarrow \quad E_{1u} = k_B T_e \cdot \ln\left\{\frac{A_{ul} d_{1u}(p_u)}{\lambda_{ul} I_{ul} \sum_{u\rangle l} A_{ul}}\right\} + \text{constant}$$

3. Variation of T_{ex} and T_e with RF pulse condition

OES SPECTRUM: Examples in DC synchronized condition

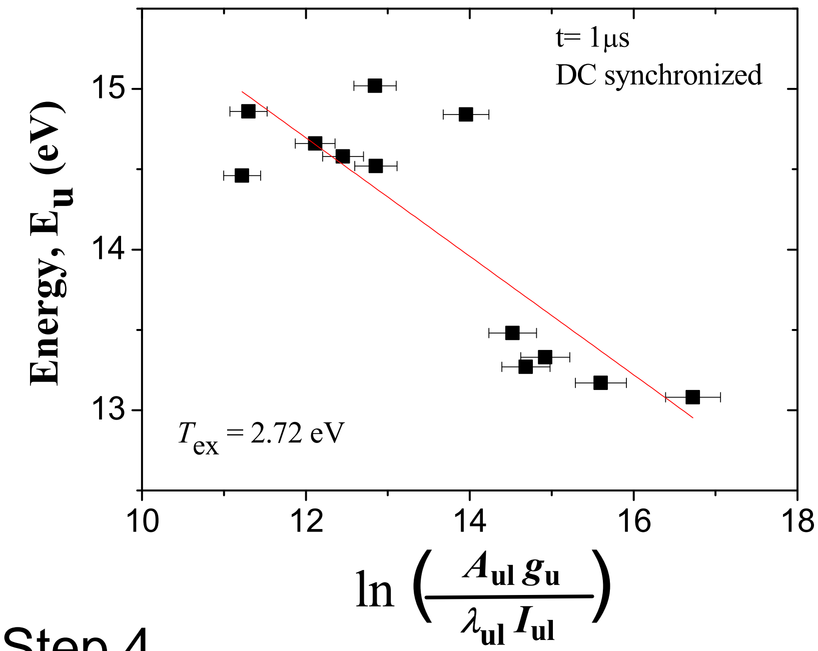
Typical OES spectrum during glow (pulse on) at t = 1 μs and after glow (pulse off) at t = 63 μs





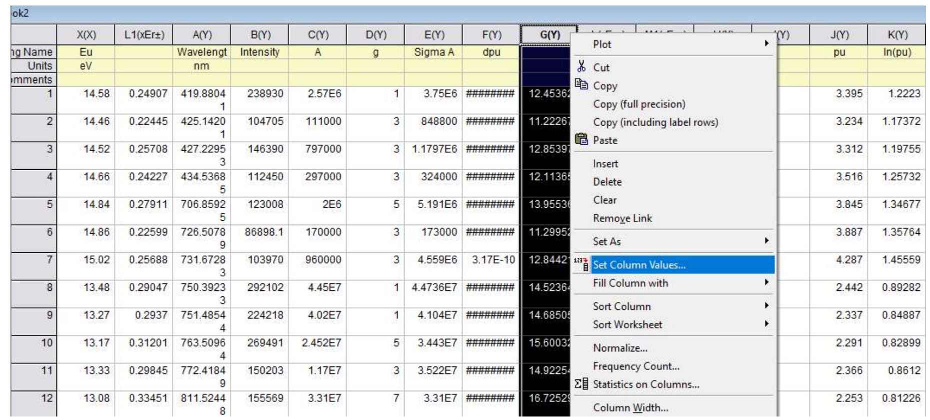
λ(Table I) Used for the calculation	λ (measured)	I(nm) At t = 1μs	I(nm) At t = 63μs
419.83	419.88041	238930	203036
425.12	425.14201	104705	108210
427.22	427.22953	146390	138939
434.52	434.53685	112450	102979
706.87	706.85925	123008	100958
726.52	726.50789	86898.1	84696.4
731.67	731.67283	103970	84518.8
750.39	750.39233	292102	151900
751.47	751.48544	224218	151487
763.51	763.50964	269491	131890
772.42	772.41849	150203	141566
811.53	811.52448	155569	95117

T_{ex} estimation using modified Boltzmann equation

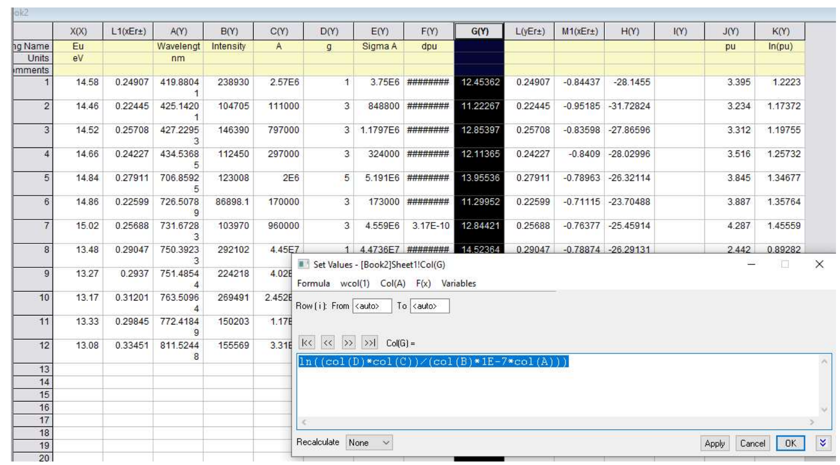


Calculation method (as a proof)

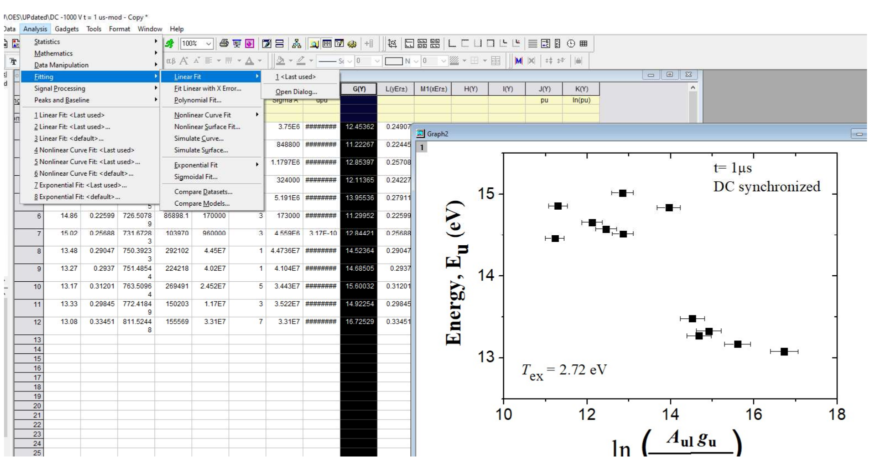
Step 1



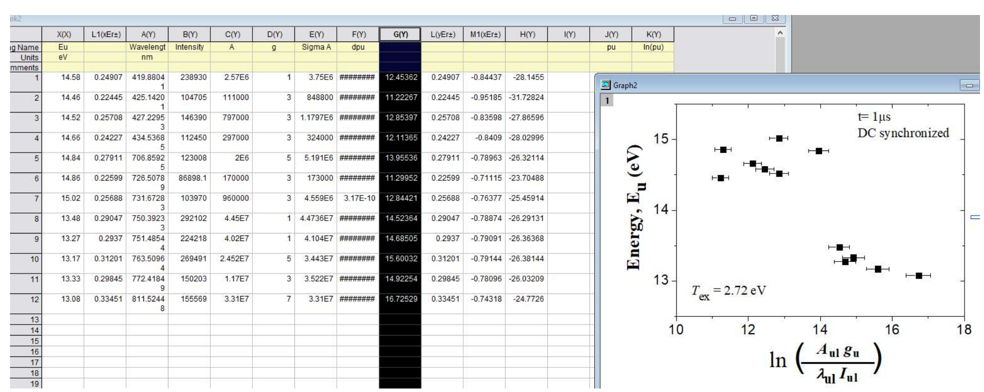
Step 2



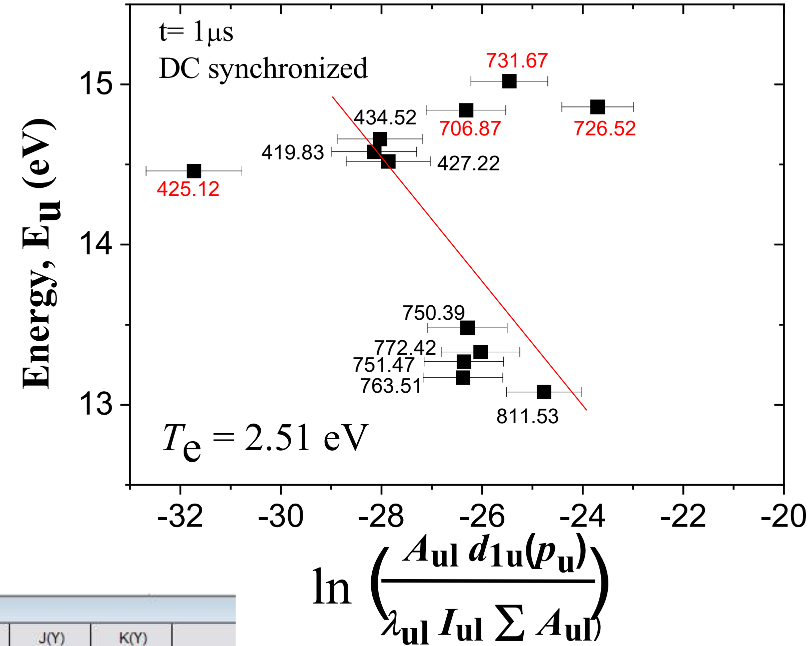
Step 4



Step 3



T_e estimation from Eqn. 11



ok2

	X(X)	L1(xEr±)	A(Y)	B(Y)	C(Y)	D(Y)	E(Y)	F(Y)	G(Y)	L(yEr±)	M1(xEr±)	H(Y)	I(Y)	J(Y)	K(Y)
ng Name	Eu		Wavelengt	Intensity	A	g	Sigma A	dpu						pu	ln(pu)
Units	eV		nm												
mments															
1	14.58	0.24907	419.88041	238930	2.57E6	1	3.75E6	########	12.45362	0.24907	-0.84437	-28.1455		3.395	1.2223
2	14.46	0.22445	425.14201	104705	111000	3	848800	########	11.22267	0.22445	-0.95185	-31.72824		3.234	1.17372
3	14.52	0.25708	427.22953	146390	797000	3	1.1797E6	########	12.85397	0.25708	-0.83598	-27.86596		3.312	1.19755
4	14.66	0.24227	434.53685	112450	297000	3	324000	########	12.11365	0.24227	-0.8409	-28.02996		3.516	1.25732
5	14.84	0.27911	706.85925	123008	2E6	5	5.191E6	########	13.95536	0.27911	-0.78963	-26.32114		3.845	1.34677
6	14.86	0.22599	726.50789	86898.1	170000	3	173000	########	11.29952	0.22599	-0.71115	-23.70488		3.887	1.35764
7	15.02	0.25688	731.67283	103970	960000	3	4.559E6	3.17E-10	12.84421	0.25688	-0.76377	-25.45914		4.287	1.45559
8	13.48	0.29047	750.39233	292102	4.45E7	1	4.4736E7	########	14.52364	0.29047	-0.78874	-26.29131		2.442	0.89282
9	13.27	0.2937	751.48544	224218	4.02E										
10	13.17	0.31201	763.50964	269491	2.452E										
11	13.33	0.29845	772.41849	150203	1.17E										
12	13.08	0.33451	811.52448	155569	3.31E										
13															
14															
15															
16															
17															
18															
19															
20															

Set Values - [Book2]Sheet1!Col(H)

Formula wcol(1) Col(A) F(x) Variables

Row (i): From <auto> To <auto>

|<< << >> >>| Col(H) =

```
ln((col(C)*col(F))/(col(A)*1e-7*Col(B)*col(E)))
```

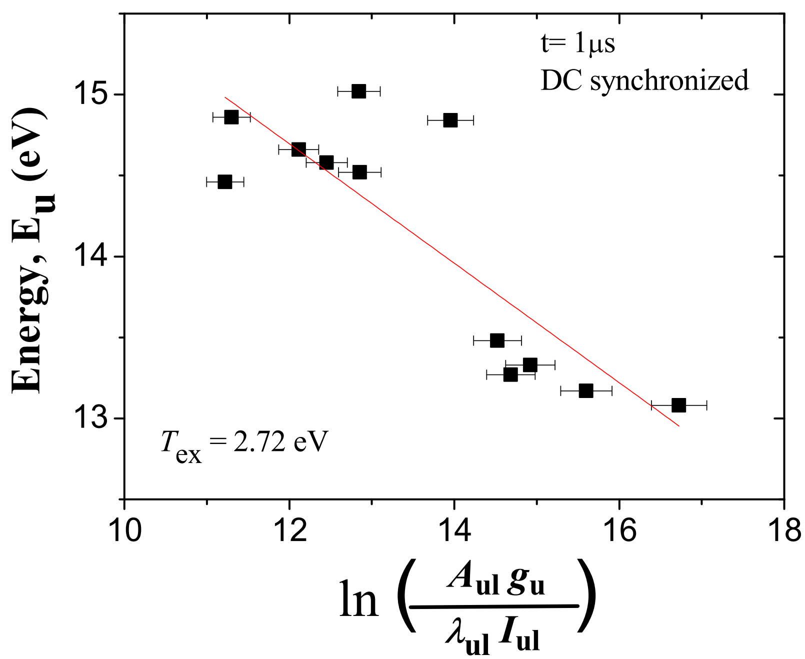
Recalculate None

Apply Cancel OK

Evaluation of T_{ex} and T_e: DC bias: -1000 V (RF-on)

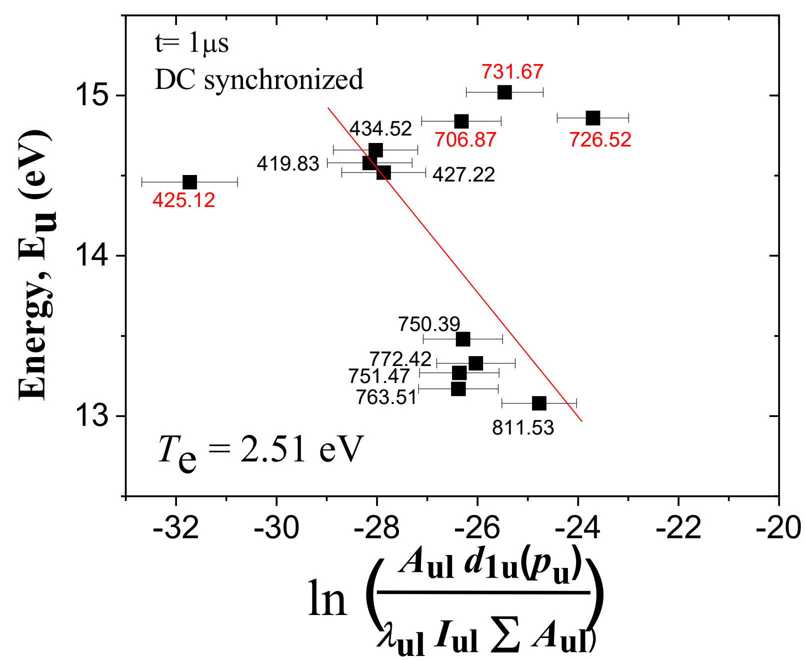
Representative plots

Electron excitation temperature



$$\frac{E_u}{k_B T_{ex}} = \ln\left(\frac{g_u \cdot A_{ul}}{I_{ul} \cdot \lambda_{ul}}\right) + \text{constant}$$

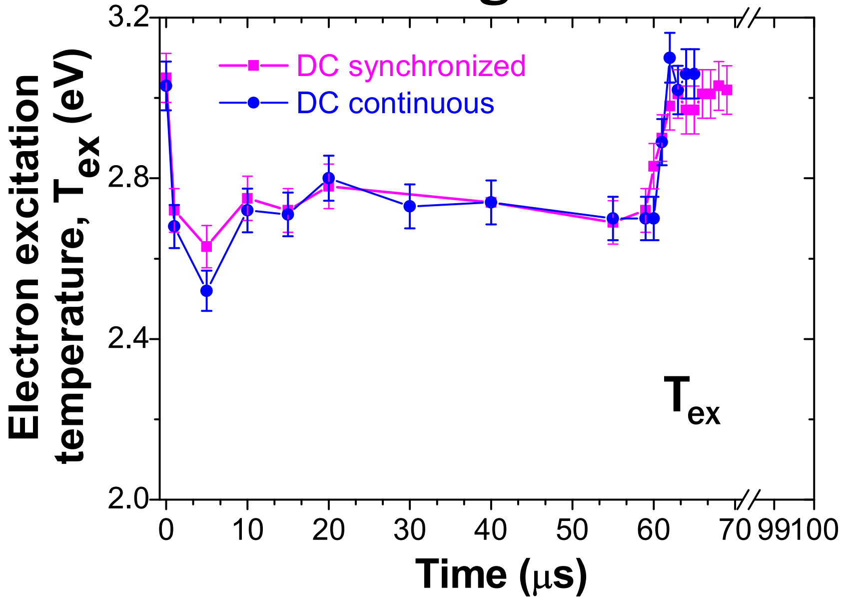
Electron temperature

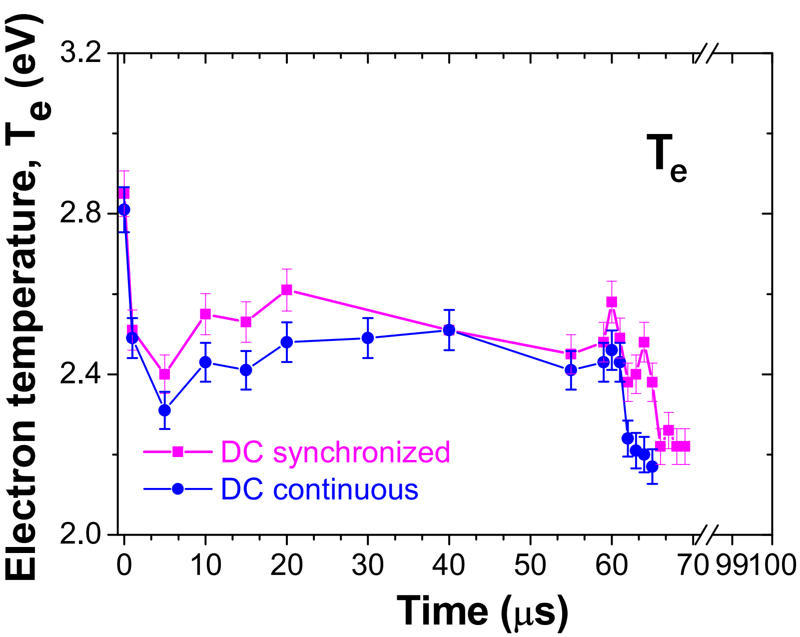


$$\frac{E_{1u}}{k_B T_e} = \ln\left\{\frac{A_{ul} d_{1u}(p_u)}{\lambda_{ul} I_{ul} \sum_{u \rangle l} A_{ul}}\right\} + \text{constant}$$

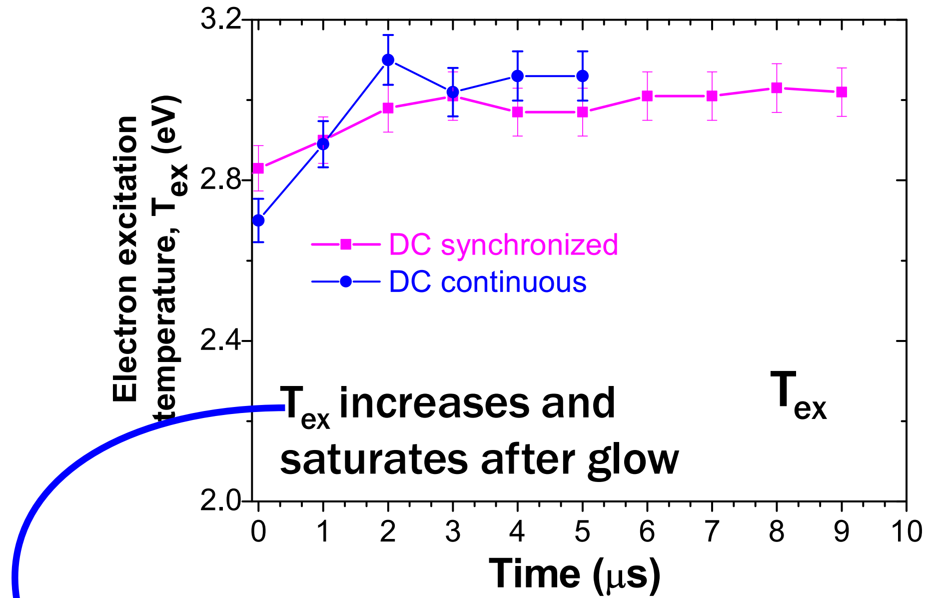
Time evolution of parameters: T_{ex} and T_e

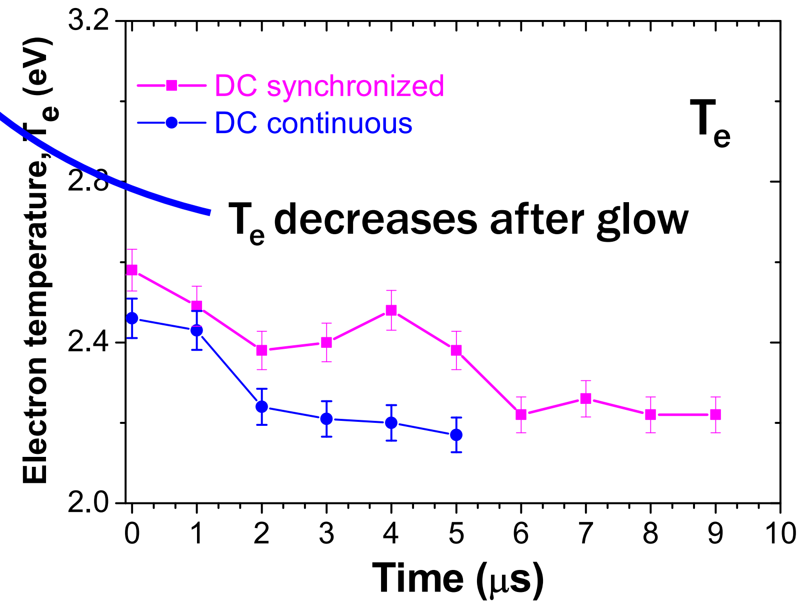
Time variation: During glow and after glow





Time variation: During glow and after glow





Determination of Plasma density (n_e) from OES data

1. The Saha equation (or equilibrium) describes the degree of ionization for any gas in thermal equilibrium as a function of the temperature, density, and ionization energies of the atoms

2. Maxwell–Boltzmann distribution is used for describing particle in plasma (as a fluid), where the particles exchange energy and momentum with each other or with their thermal environment.

- Formulation of equation for n_e using Saha and Maxwell-Boltzmann equations
- Variation of n_e with RF pulse condition

Plasma density (n_e) evaluation using Saha ionization equation

We approach the Saha equation through the Einstein transition probabilities while making use of the Boltzmann equation.

- **We consider two lines: 419.83 nm (Ar atom) and 423.72 nm (Ar^+) to determine n_e. Applying Boltzmann equation, we get the line intensity ratio as**

$$\frac{I_{419.83}}{I_{423.72}} = \left(\frac{\lambda_{423.72} \cdot A_{419.83} \cdot N_{419.83} \cdot g_{419.83} \cdot U_{423.72}(T_e)}{\lambda_{419.83} \cdot A_{423.72} \cdot N_{423.72} \cdot U_{419.83}(T_e)} \right) \cdot \exp\left(- \frac{E_{419.83} - E_{423.72}}{k_B T_e} \right) \quad (13)$$

The subscript 419.83 and 423.72 represents the emissions from Ar atom and ions, respectively.
$N_{419.83}$ and $U_{419.83}$ = densities of excited atoms and partition function relevant to emissions of wavelength 419.83 nm
$N_{423.72}$ and $U_{423.72}$ = densities of excited atoms and partition function relevant to emissions of wavelength 423.72 nm

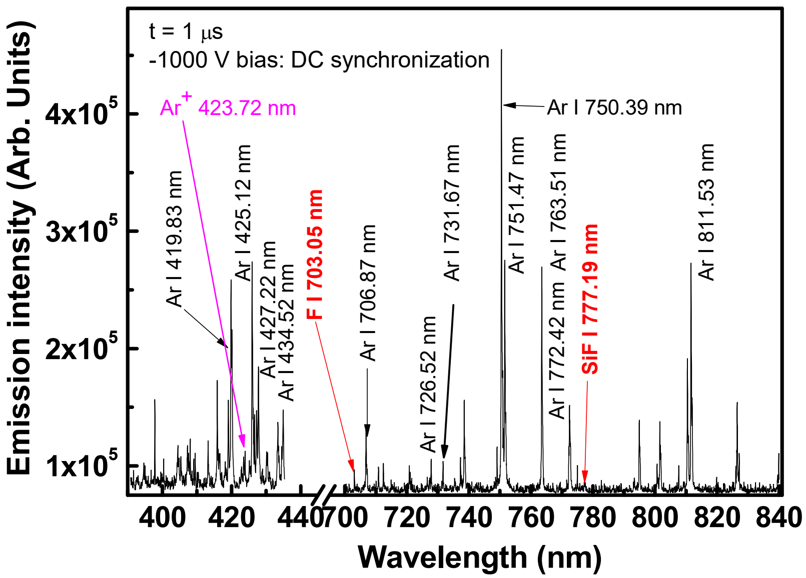
Applying Saha equation, we get the number density ratio involving atomic excitation and ionization as

$$\frac{n_e N_{423.72}}{N_{419.83}} = \frac{2U_{423.72}(T_e)}{U_{419.83}(T_e)} \cdot \frac{(2\pi m_e k_B T_e)^{3/2}}{h^3} \cdot \exp\left(- \frac{E_{Ar} - \Delta E_{Ar}}{k_B T_e} \right) \quad (14)$$

Substituting Eqn. (14) in Eqn. (13), we get the expression for plasma density as

$$n_e = 2 \cdot \frac{(2\pi m_e k_B)^{3/2}}{h^3} \left(\frac{I_{419.83} \cdot A_{423.72} \cdot g_{423.72} \cdot \lambda_{419.83}}{I_{423.72} \cdot A_{419.83} \cdot g_{419.83} \cdot \lambda_{423.72}} \right) \cdot T_e^{3/2} \exp\left(\frac{-E_{Ar} + \Delta E_{Ar} + E_{423.72} - E_{419.83}}{T_e} \right) \quad (15)$$

Plasma density (n_e) evaluation using Saha ionization equation



- Two select lines from our measurements 419.83 nm (Ar atom) and 423.72 nm (Ar^+) are chosen to (n_e).
- We need the value of T_e to calculate n_e

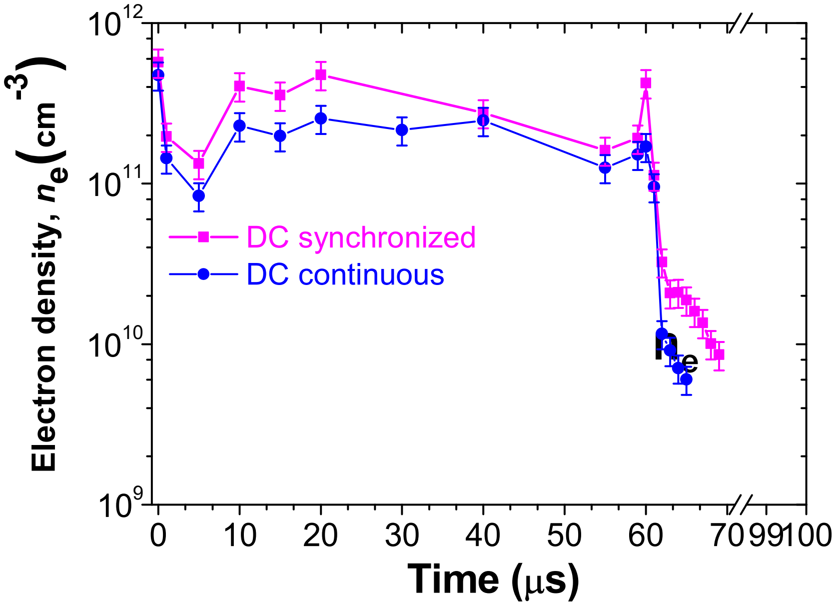
$$n_e = 2 \cdot \frac{(2\pi m_e k_B)^{3/2}}{h^3} \left(\frac{I_{419.83} \cdot A_{423.72} \cdot g_{423.72} \cdot \lambda_{419.83}}{I_{423.72} \cdot A_{419.83} \cdot g_{419.83} \cdot \lambda_{423.72}} \right) \cdot T_e^{3/2} \exp\left(\frac{-E_{Ar} + E_{423.72} - E_{419.83}}{T_e} \right) \quad (15)$$

Wavelength λ (nm)	Parameters	Emission intensity	Other Comments
Ar I-419.83	$g_{419.83}$ = 1; $E_{419.83}$ = 14.58 eV $A_{419.83}$= 0.257 x 10^7 s^{-1}	$I_{419.83}$ = measured intensity of 419.83 nm line	E_{Ar} = 15.76 eV
Ar^+-423.72	$g_{423.72}$ = 4; $E_{423.72}$ = 37.11 eV $A_{423.72}$= 1.12 x 10^7 s^{-1}	$I_{419.83}$ = measured intensity of 423.72 nm line	

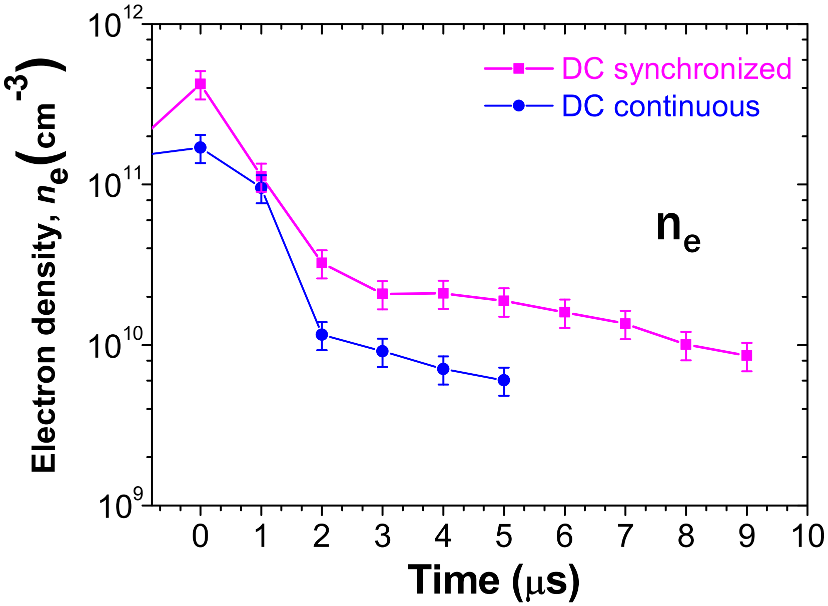
<u>Data taken from</u>: W. L. Wiese, M. W. Smith and B. M. Miles, Atom. Trans. Prob. NSRDS-NBS. 22 (US), 1969.

Time evolution of parameters: T_{ex} and T_e

Time variation: During glow and after glow



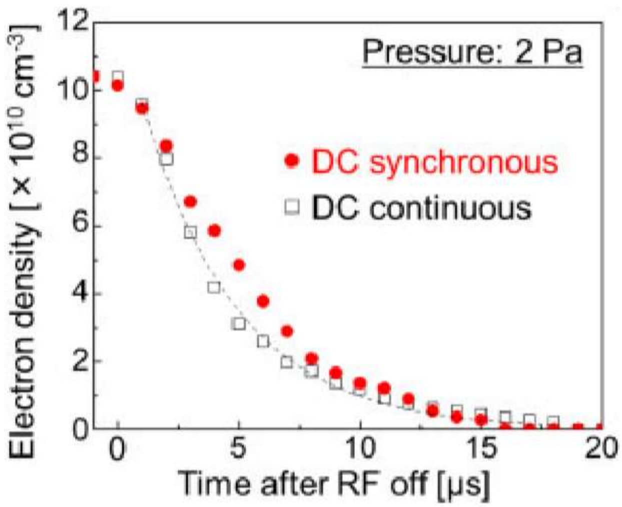
Time variation: During glow and after glow



n_e falls rapidly in DC continuous mode compared to that of DC synchronized mode.

Comparison with earlier low power and different gas flow experiment

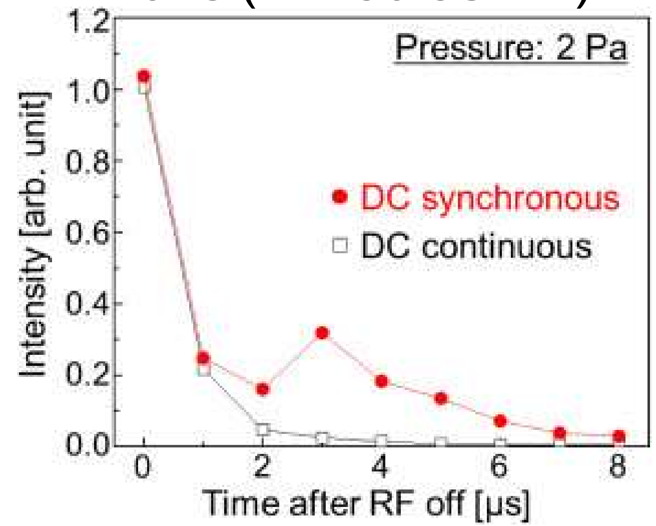
n_e= decay rate of ~ 4.0 × $10^5 s^{-1}$



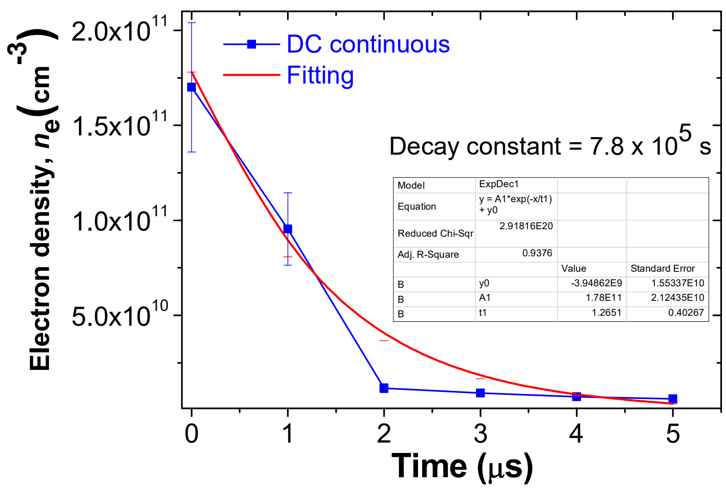
Earlier experiment: Different gas flow by Surface wave probe
40 MHz/3 MHz powers = 1000 W/2000 W
$Ar/O_2/C_4F_8$ flow rate in sccm = 100/100/100

Earlier experiment:

OES (Ar 750.38 nm)



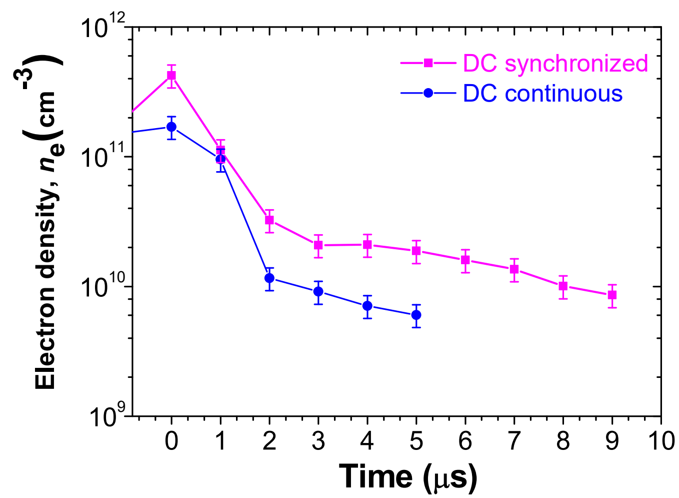
Ohya et al. Jpn. J. Appl. Phys. 56, 06HC03 (2017)



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	2.91816E20		
Adj. R-Square	0.9376		
		Value	Standard Error
B	y0	-3.94862E9	1.55337E10
B	A1	1.78E11	2.12435E10
B	t1	1.2651	0.40267

We can not make exponential fit for the case of DC synchronized case.

Present experiment:



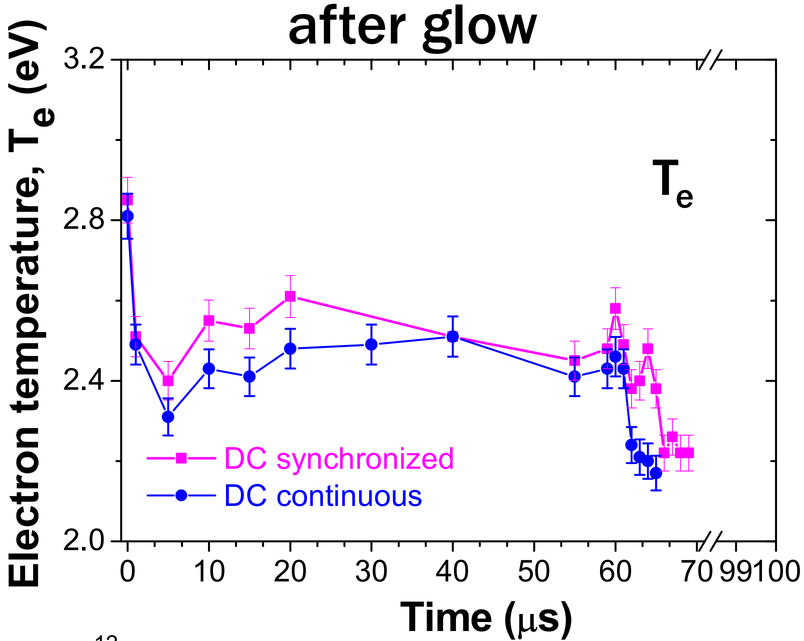
Present experiment: Ar rich plasma by OES
40 MHz/3 MHz powers = 1000 W/2000 W
$Ar/O_2/C_4F_8$ flow rate in sccm = : 300/30/60

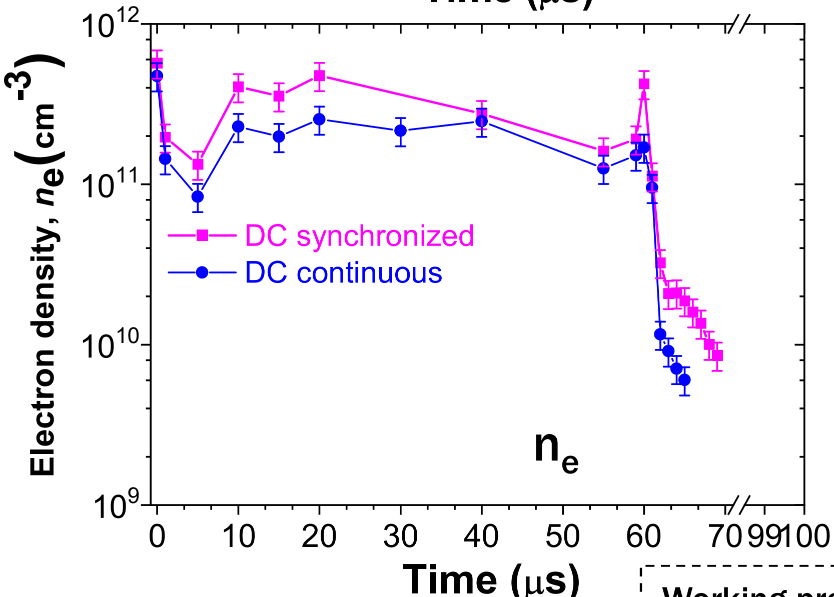
Summary / Conclusion

- Scientific aspect
- Relevance to etching process
- Relevance to corona approximation

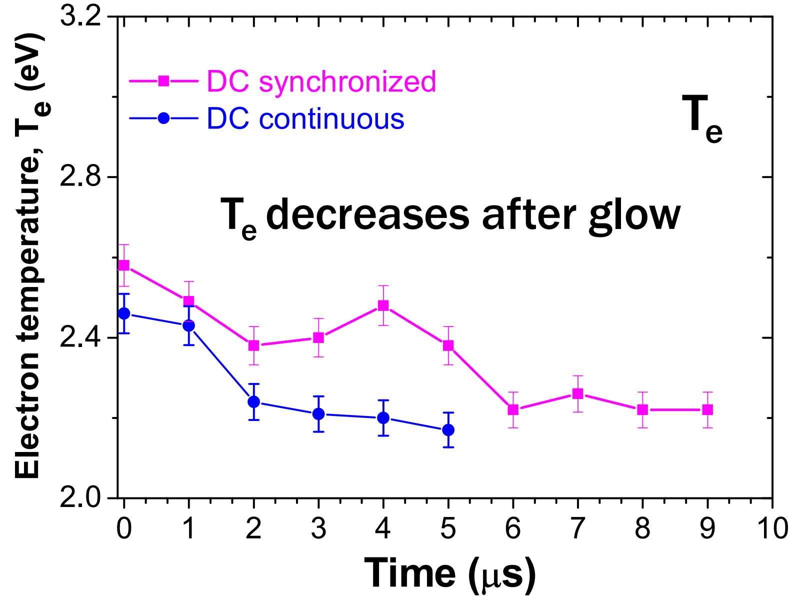
Overall variation of T_e and n_e with pulse

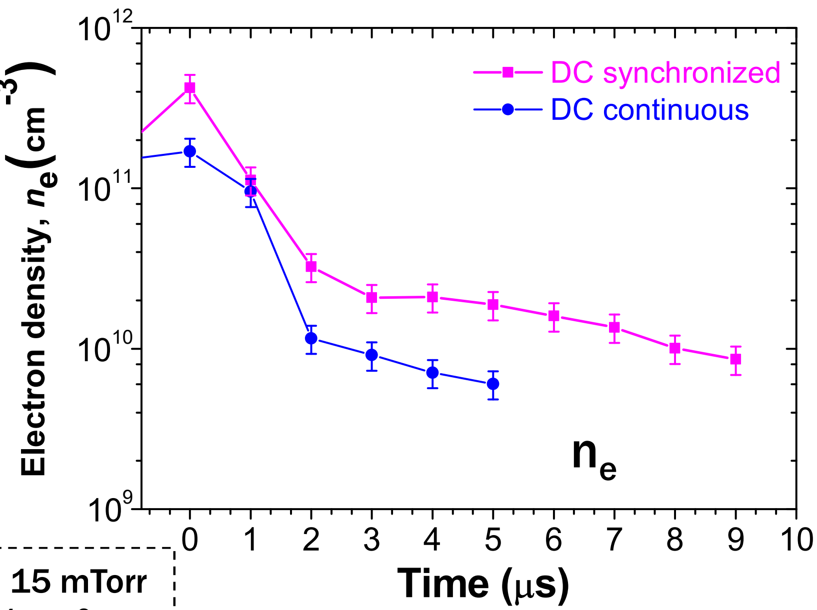
Time variation: During glow and after glow





Time variation: During glow and after glow





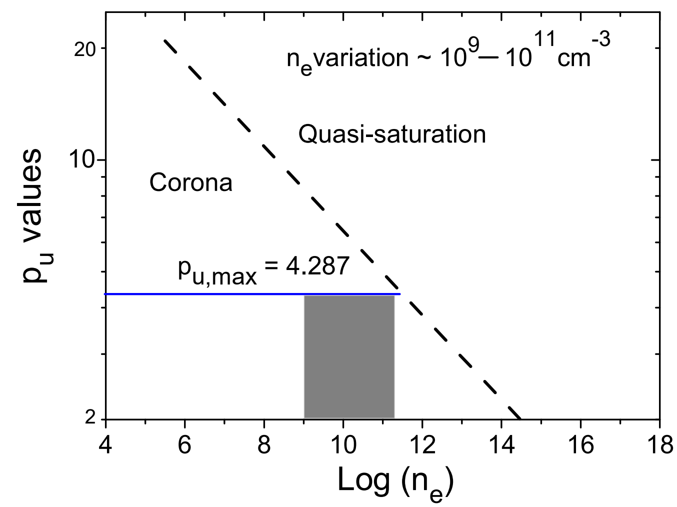
Working pressure = 2Pa = 15 mTorr
Neutral density = 4.8 x10^{14} cm^{-3}
Plasma density ~ 10^9 - 10^{11} cm^{-3}

Kinetics of Plasma: Validation of Corona Approximation

Comparison of our experimental data with Fujimoto’s work

- The electron density (n_e) in the system of excited levels determines the population density of all exited levels represented by the effective principal quantum number p_u.
- Fujimoto,[14] in his work, has determined the dependence of p_u on n_e by the phase diagram.
- Phase diagram shows three stages of plasmas including the corona phase.
- Data in our experiments show that
  $2 < p_u < 4.3$ (Table 1)
  n_e (maximum) ~ 10^{11} cm^{-3}

Dependence of p_u on n_e



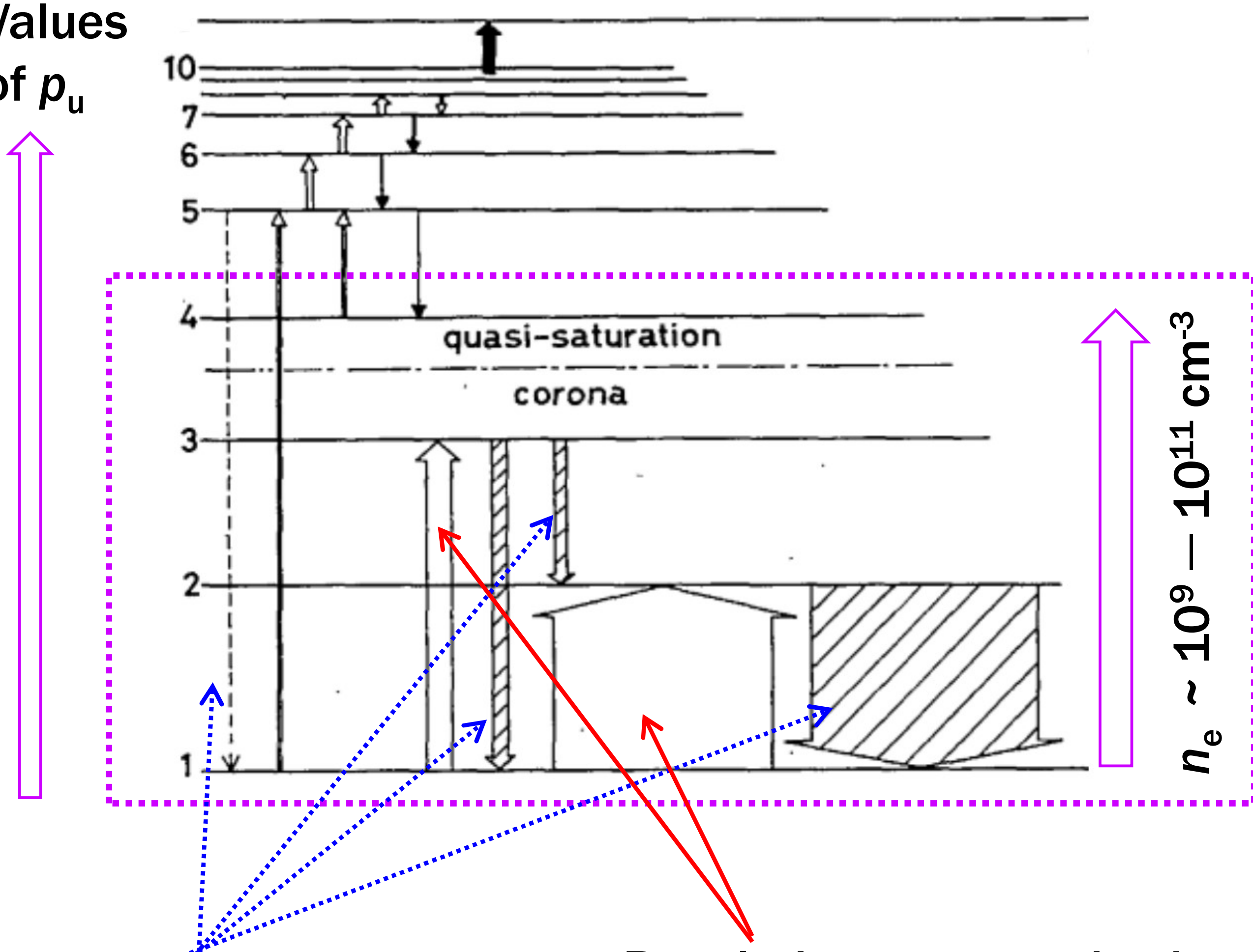
J. Phys. Soc. Japan 47, 273 (1979).

The present results suits favorably with the corona stage, and hence, corona approximation is well validated

Kinetics of Plasma: Phase diagram for our measurements

Flow of electrons in the energy level phase diagram for our measurements

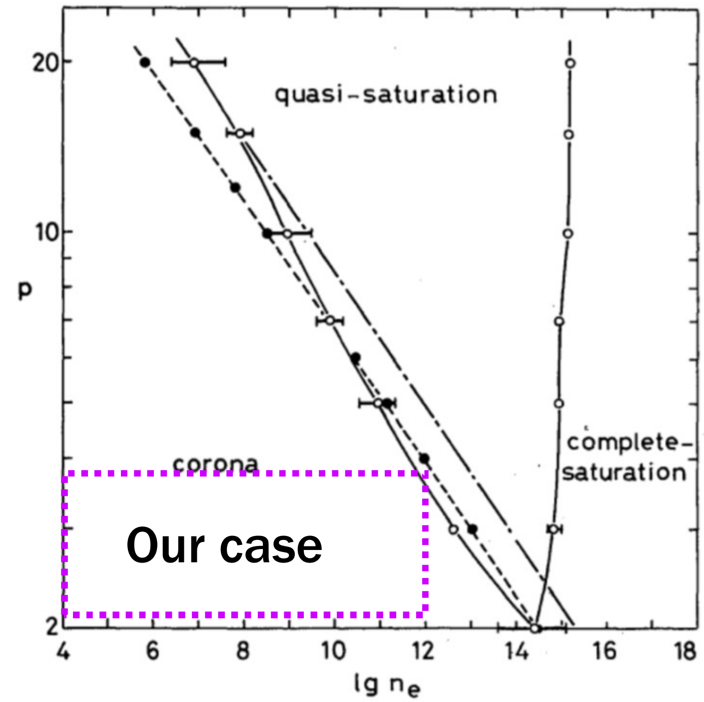
Values of p_u



Radiative transition (De-populating process)

Fujimoto's work

Dependence of p_u on n_e

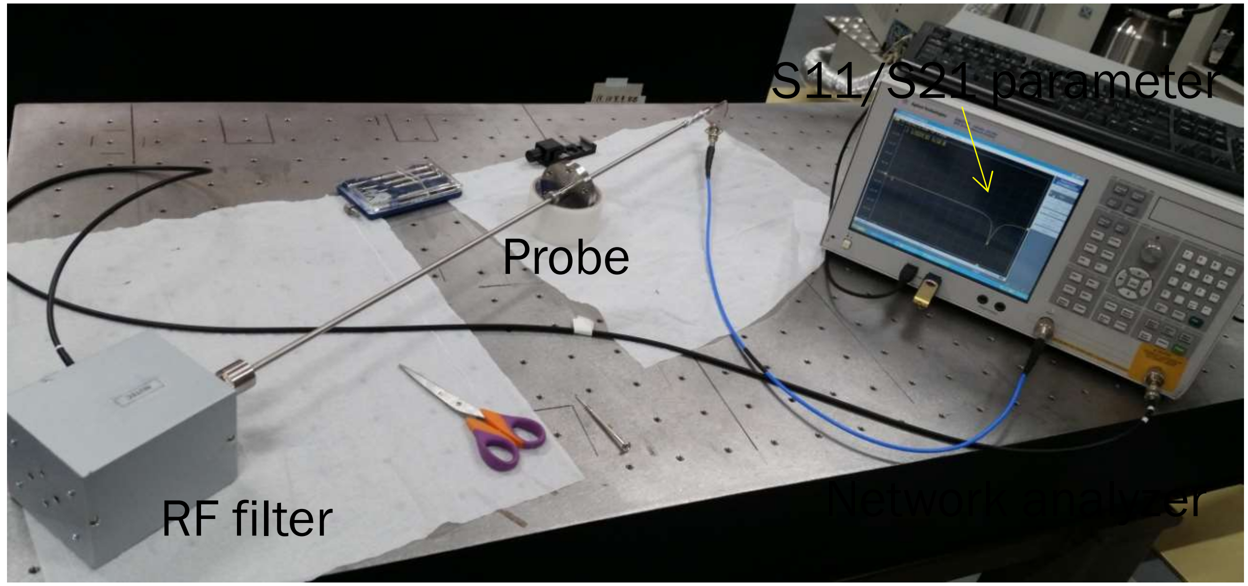


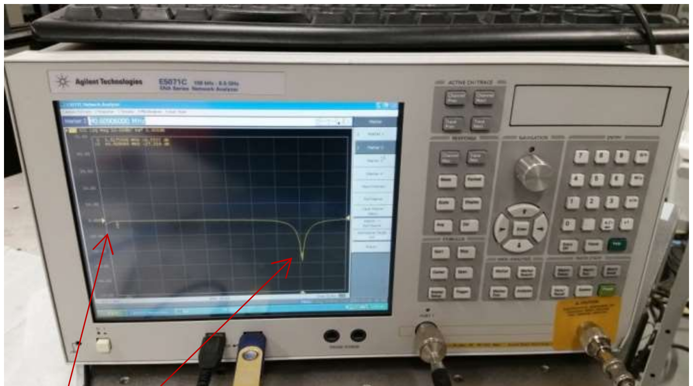
J. Phys. Soc. Japan 47, 273 (1979).

Populating process is dominantly by the direct excitation from the ground (p_u = 1) level, while the small contribution comes from the cascade from higher levels (p ≥ 5), which are not observed in OES experiments.

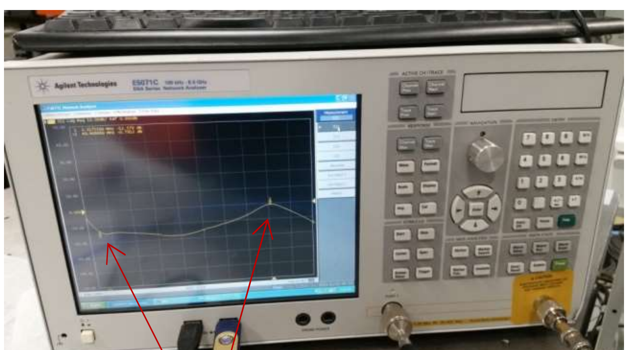
S11/S21 parameters monitoring for Filter tuning: for NUTEC system

Tuning for ~ 40.68 MHz &
3.2 MHz





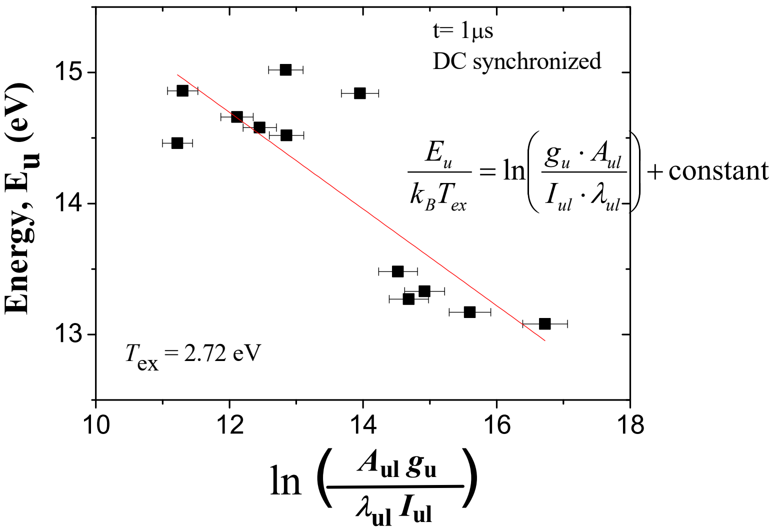
S_{21} parameter at two excited frequencies.



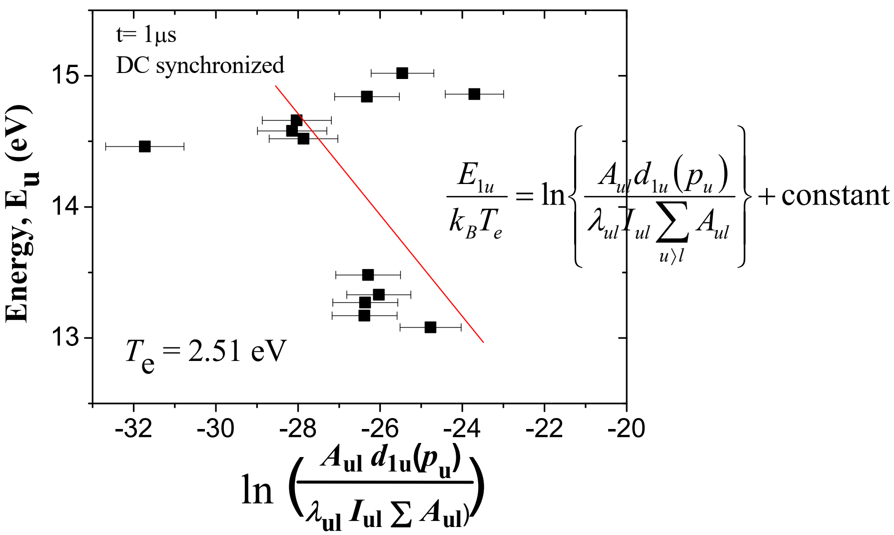
S_{11} parameter at two frequencies

LP I-V data Measurement: Validation our OES data using RF compensated Langmuir probe

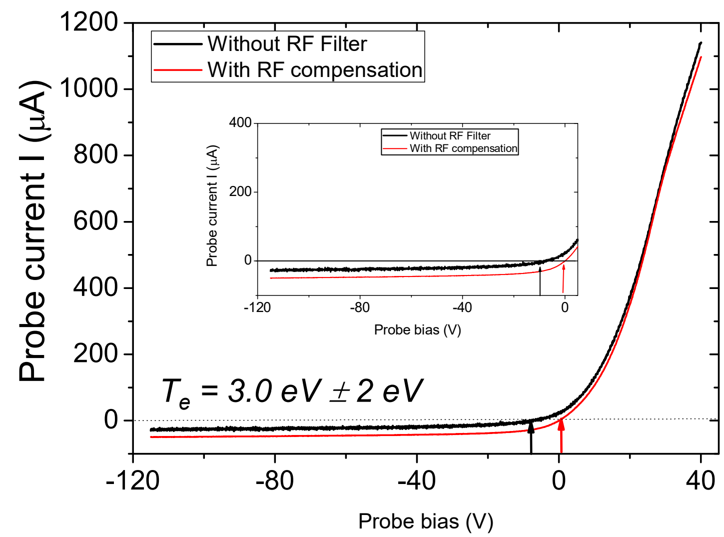
RF compensating Filter circuit



We will report our work on detailed design of RF Langmuir probe and LP measurements in future work.



LP measurement in discharge at 1 μs



Conclusion

1. Spectroscopic study in dual frequency commercial CCP plasmas at low-pressure is undertaken for an etching process.

2. Corona plasma approximation is realized for our operating condition of low pressure plasma with low to moderate plasma density.

3. Plasma parameters like T_e and n_e were determined in relation to the Applied RF pulsed power.

4. Over the course of one pulse period it is observed that both T_e and n_e increases during on-phase and decays during the off-phase. Both T_e and n_e are synchronized with the RF pulse.

5. In RF pulse off phase, most electron disappears and negative ions can be expected to generate by the electron attachment process to maintain the plasma neutrality by positive and negative ions.

6. In pulsed CCP plasmas during the RF off-period, T_e drops while maintaining the plasma of very low n_e. T_e in the Synchronized phase enhances compared to continuous mode due to higher electronegativity in afterglow.

7. Corona plasma approximation is well validated by the experimental results.

Thank you !