Formulation of a Global Model for C_8H_9Cl Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics

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Summarization

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Topic

Formulation of a Global Model for C_8H_9Cl Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics

Experiment

- Back ground
- Approach
- Result

Measurement of dominant product in C_8H_9Cl plasma

← Christina

Simulation

- Approach
- Result

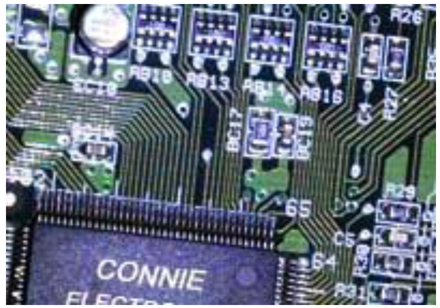
Calculation of rate constant for each reaction

← Robert David

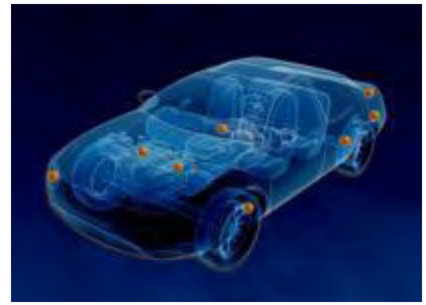
1. Back ground

Polymer coating Applications

Medical



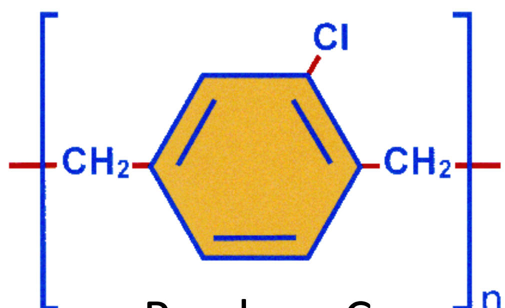
Electronics



Car

Air crafts/Space Science

Parylene C is a widely used polymer



Parylene C

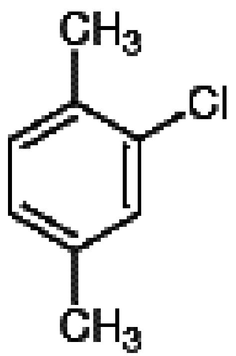
Properties

- very thin
- high water proof
- high chemical proof
- Gas imperviableness
- high insulation properties
- high burning resistance

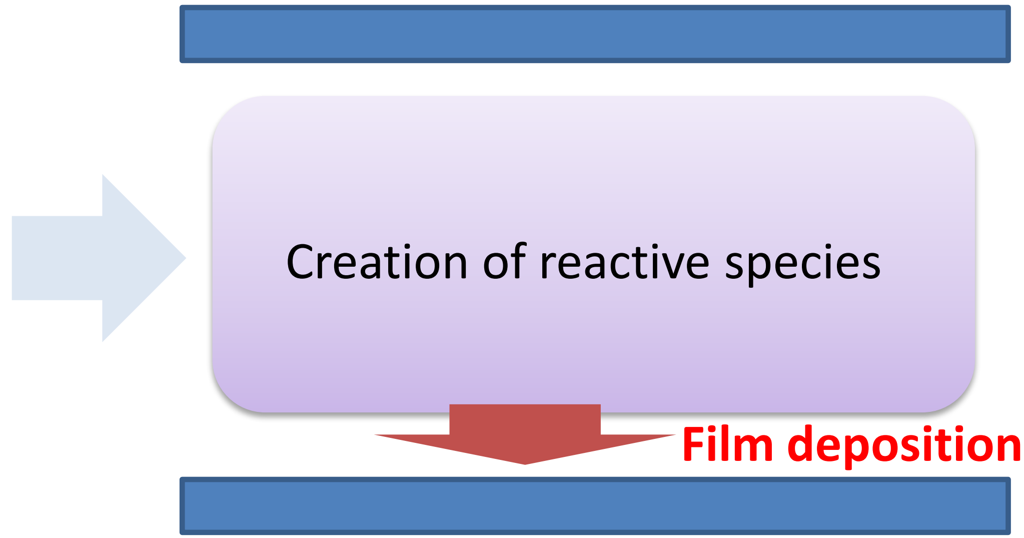
<u>In almost all points, Parylene has better properties than the others organic coating</u>

1. Back ground

How to make a Parylene C coating



C_8H_9Cl



High power		Low power
Excellent adhesion!!	⇔	Better functionality!!

Plasma polymerization and film deposition are strongly coupled

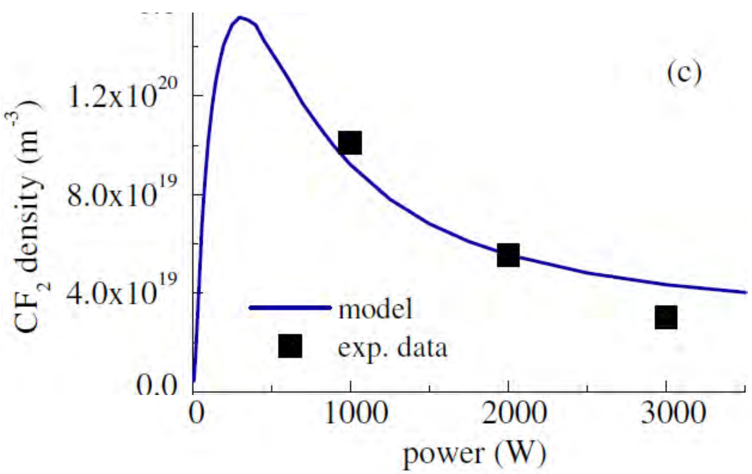
1. Back ground

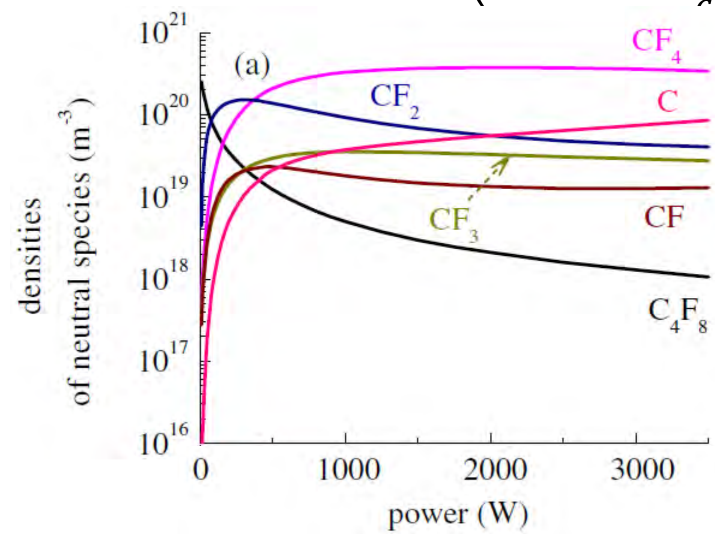
The generic mass balance at the steady state

$$0 = \frac{Q_{f,i}}{V k_B T_0} - \frac{S_p}{V} n_i + \sum_{j=1}^{n_{r,gas}} R_{i,j}^{gas} + \sum_{k=1}^{n_{r,surf}} R_{i,k}^{surf} \qquad 0 = \sum_{k=1}^{n_{r,surf}} R_{m,k^{surf}}$$

The generic power balance at the steady state

$$0 = \frac{P_{abs}}{V} + \sum_{j=1}^{n_{r,gas}} R_{e,j}^{gas} \varepsilon_{loss,j} + \sum_{k=1}^{n_{r,surf}} R_{c,k}^{surf} (\varepsilon_{ion,w} + \varepsilon_{ion,w}) + \frac{S_p}{V} \frac{3}{2} \left(n_e k_B T_e + \sum_{c=1}^{n_c} n_{+,c} k_B T_{ion} \right)$$





production rate of species have to be known to solve this equations

[1] G Kokkoris, A Goodyear, M Cooke and E Gogolides, "Global Model for C4F8 Plasma Coupling Gas Phase & Wall Surface Reaction Kinetices", J. Phys. D: Appl. Phys. **41**, 195211 (2008)

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Formulation of a Global Model for C_8H_9Cl Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics

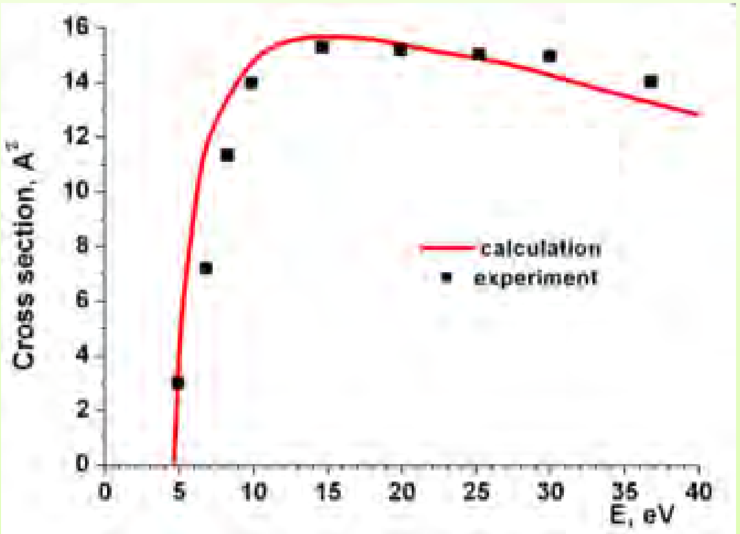
Rate constants
(for Most important chemical reactions)

$$k_v = aT_e^b exp\left(-\frac{c}{T_e}\right)$$ [1]

Calculate from Cross Sections

$$K(T_e) = \left(\frac{m}{2\pi q T_e}\right)^{\frac{3}{2}} \int_0^\infty \sigma(v) v exp\left(-\frac{mv^2}{2qT_e}\right) dv$$

Additional data from OES e-beam

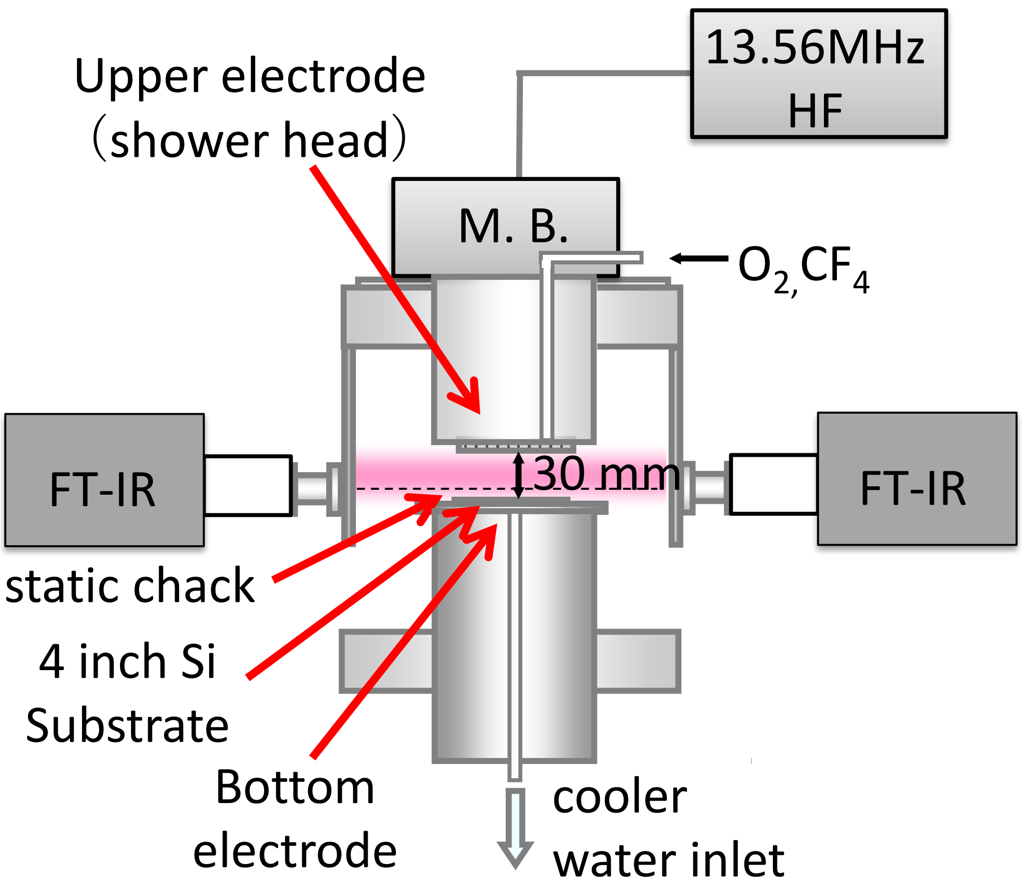


[1] G Kokkoris, A Goodyear, M Cooke and E Gogolides, "Global Model for C4F8 Plasma Coupling Gas Phase & Wall Surface Reaction Kinetices", J. Phys. D: Appl. Phys. **41**, 195211 (2008)

2. Equipment and condition

GEC cell[1]

(The Gaseous Electronics Conference RF Reference Cell)



Cleaning Condition

Gas: O_2 : 30 sccm
CF_4 : 1 sccm
Upper electrode : 300 W(13.56 MHz)
Bottom electrode : 0 W
Pressure : 30 mTorr
Time : 30 min
Temperature of chamber : 60℃

Deposition Condition

Gas: ClpX(C_8H_9Cl) : 20 sccm
Upper electrode : 100 W(13.56 MHz)
Bottom electrode : 0 W
Pressure : 15 mTorr
Time : 40 min
Temperature of chamber : 60℃
Temperature of substrate : 20℃

[1] J. K. Olthoff, K. E. Greenberg, "The Gaseous Electronics Conference RF Reference Cell-An Introduction", J. Res. Natl. Inst. Stand. Technol. **100**, (1995) 327-339

3. Fixing the GEC chamber

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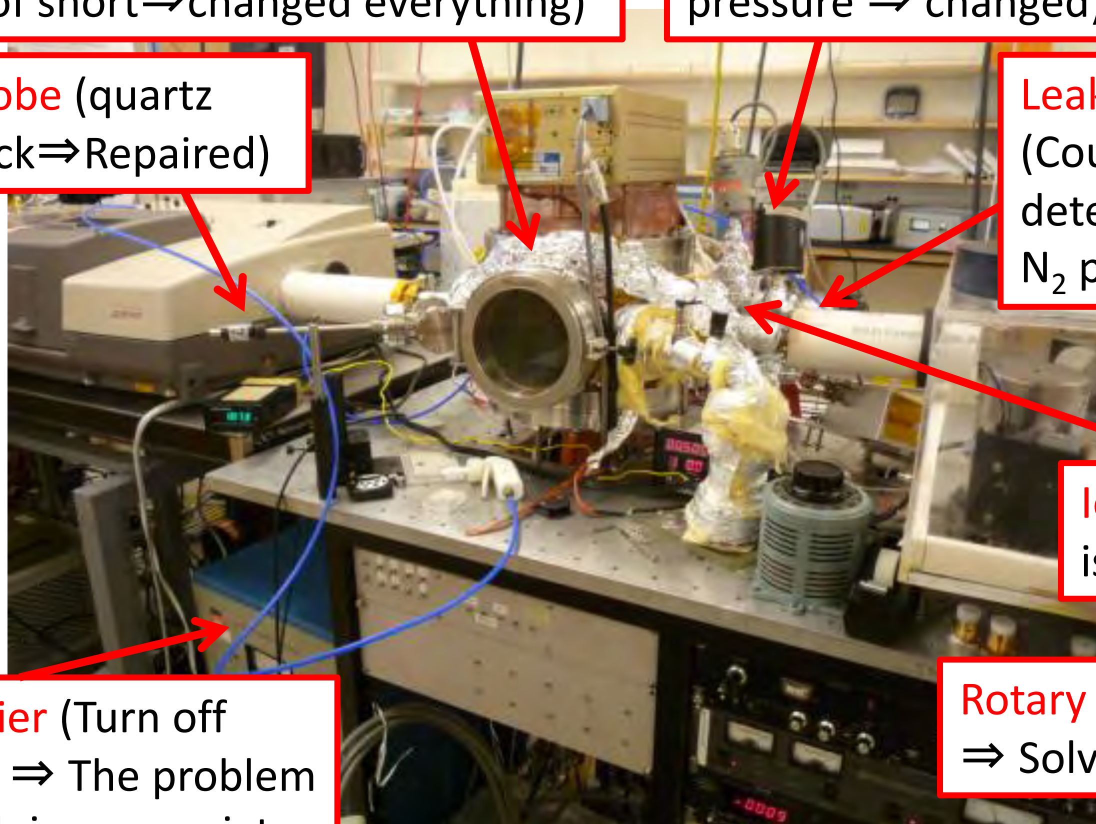
I Fixed the GEC(The Gaseous Electronics Conference RF Reference Cell) chamber. Most of the parts attached GEC chamber were broken. The reasons are unknown. The chamber wasn't used for half a year. Anyway, I fixed :



Ribbon heater (broken because of short⇒changed everything)

Barton gauge (Unavailable pressure ⇒ changed)

Floating probe (quartz tube has lack⇒Repaired)

Leakage of the chamber (Couldn't find with a leack detector ⇒ Found with N_2 pressurization)

Ion gauge (Ion gauge is Broken ⇒ Changed)

Rotary Pump (Low pumping ⇒ Solved with changing oil)

Rf power supplier (Turn off unintentionally ⇒ The problem was induce with inappropriate fuse and it is changed)

3. FT-IR spectra

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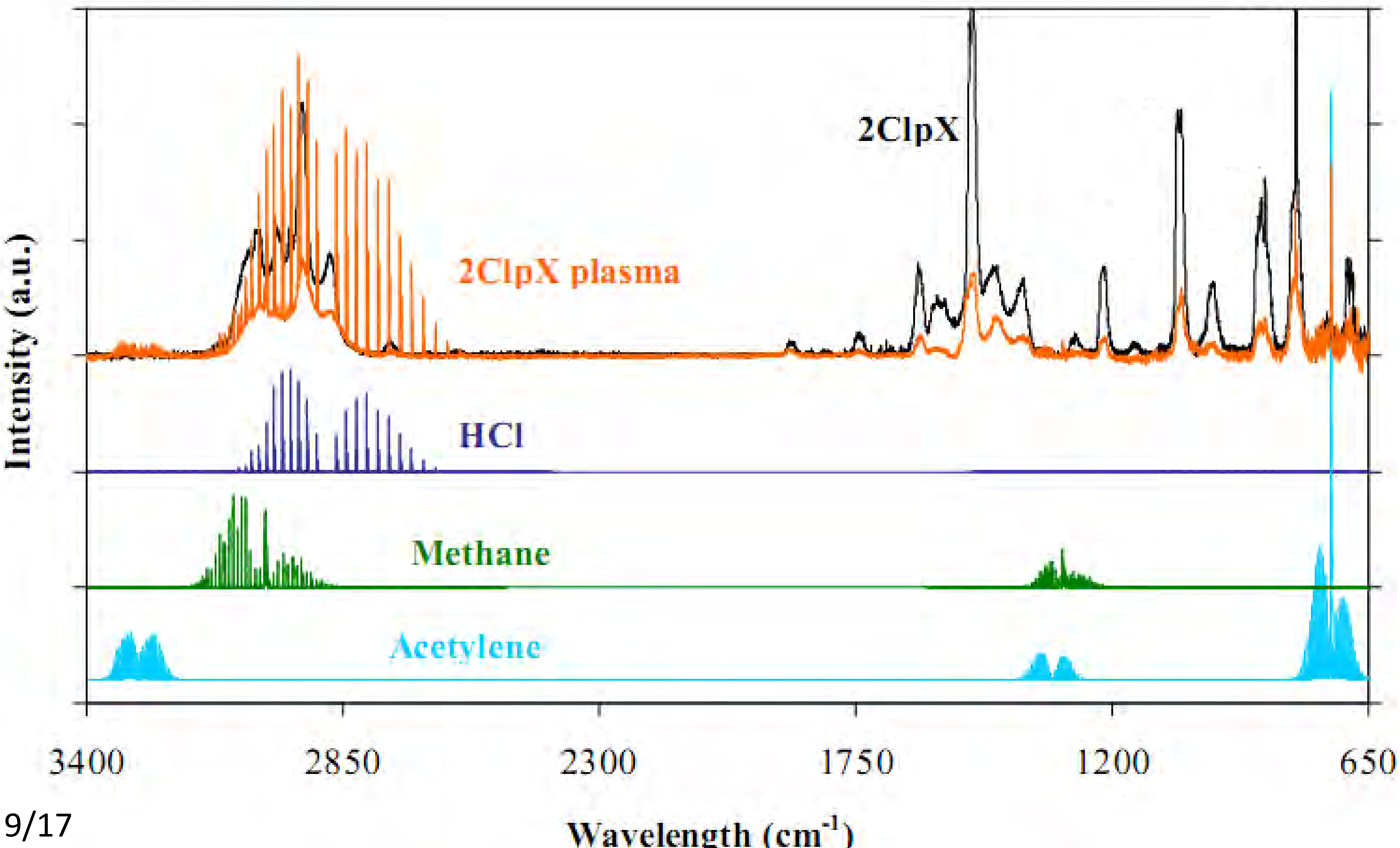
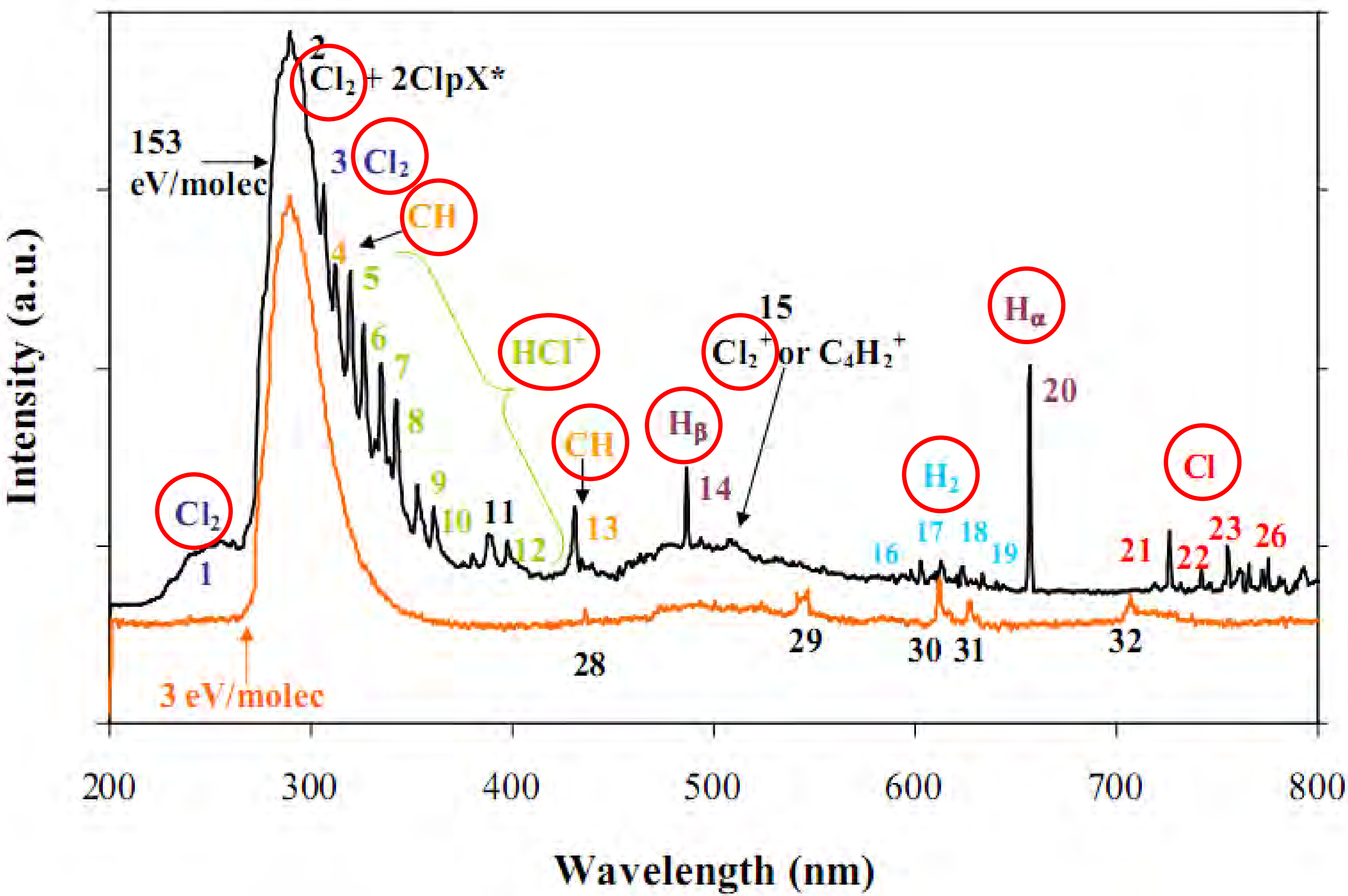
Dominant product was measured with FT-IR and OES measurement.



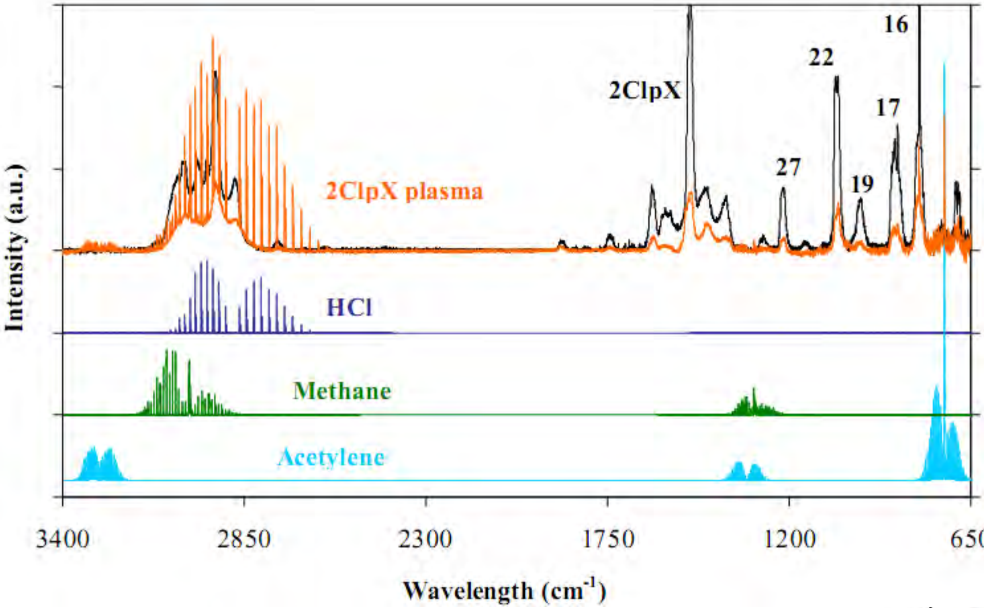
3. OES spectra



3. FT-IR and OES spectra

Hori・Sekine Lab. Nagoya University

Dominant product was measured with FT-IR and OES measurement.



FT-IR

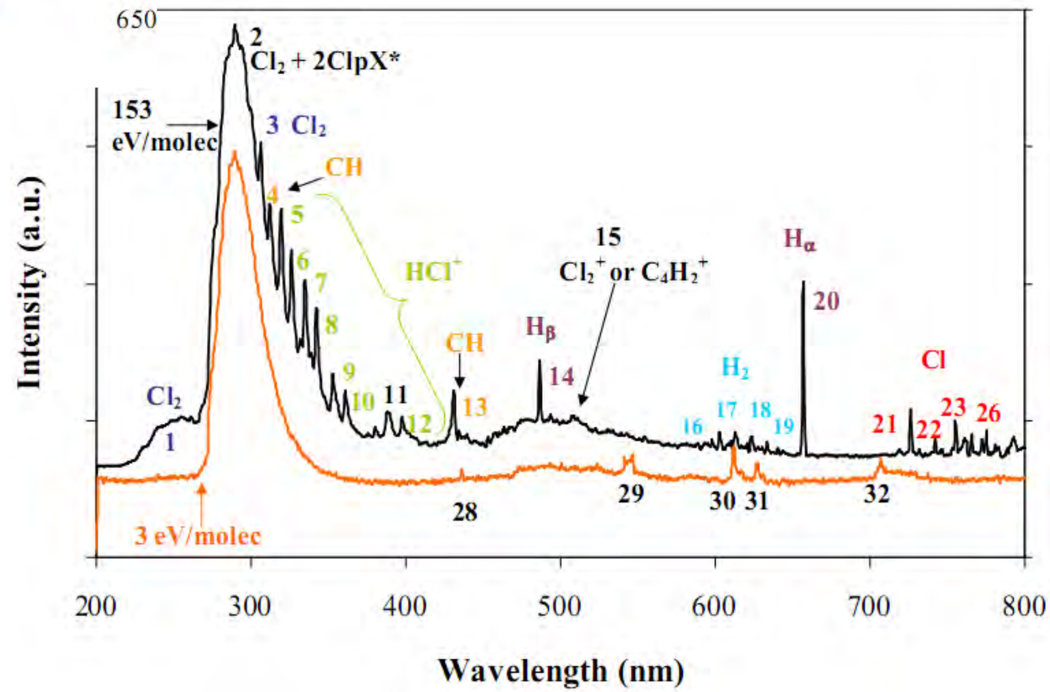
～Dissociation reaction～

- HCl
- Methane
- Acetylene

OES

～Excitation reaction～

- Cl_2/Cl
- H_2/H
- HCl
- CH



Electron impact reactions

Elastic collisions

$2ClpX + e \longrightarrow 2ClpX + e$

$HCl + e \longrightarrow HCl + e$

$CH_4 + e \longrightarrow CH_4 + e$

$C_2H_2 + e \longrightarrow C_2H_2 + e$

$H_2 + e \longrightarrow H_2 + e$

Vibrational excitation

$2ClpX + e \longrightarrow 2ClpX(v) + e$

$HCl_{v=0} + e \longrightarrow HCl_{v=1,2...} + e$

$CH_4 + e \longrightarrow CH_4(v) + e$

$C_2H_2 + e \longrightarrow C_2H_2(v) + e$

$H_2 + e \longrightarrow H_2(v) + e$

Dissociation reactions

$2ClpX + e \longrightarrow \bullet pX + \bullet Cl$

$2ClpX + e \longrightarrow \bullet ClT + \bullet CH_3$

$2ClpX + e \longrightarrow 3\bullet C_2H + 2\bullet CH_3 + \bullet Cl$

$HCl_{v=0} + e \longrightarrow H + Cl + e$

$HCl_{v=0,1,2...} + e \longrightarrow HCl^- \longrightarrow H + Cl^-$

$HCl_{v=0,1,2...} + e \longrightarrow H^- + Cl$

$HCl_{v=0,1,2...} + e \longrightarrow HCl^- \longrightarrow Cl + H^-$

$HCl_{v=0} + e \longrightarrow HCl^+ + 2e$

$Cl_2 + e \longrightarrow Cl_2^+ + 2e$

$Cl_2 + e \longrightarrow Cl^- + Cl^+ + e$

$Cl_2 + e \longrightarrow 2Cl + e$

$Cl_2 + e \longrightarrow Cl + Cl^+ + 2e$

$Cl_2 + e \longrightarrow Cl^- + Cl + e$

$Cl + e \longrightarrow Cl^+ + 2e$

$Cl + e \longrightarrow Cl^-$

$Cl^- + e \longrightarrow Cl + 2e$

$H_2 + e \longrightarrow 2H + e$

$H_2 + e \longrightarrow H_2^+ + 2e$

$H_2 + e \longrightarrow 2H^+ + 2e$

$CH_4 + e \longrightarrow CH_4^+ + 2e$

$CH_4 + e \longrightarrow CH_3^+ + H + 2e$

$CH_4 + e \longrightarrow CH_2^+ + H_2 + 2e$

$CH_4 + e \longrightarrow CH^+ + H_2 + H + 2e$

$CH_4 + e \longrightarrow CH(A^2\Delta) + H_2 + H + e$

$CH_4 + e \longrightarrow CH(A^2\Delta) + 3H + e$

$C_2H_2 + e \longrightarrow C_2H_2^+ + 2e$

$C_2H_2 + e \longrightarrow CH^+ + CH + 2e$

$C_2H_2 + e \longrightarrow C_2H + H + e$

$C_2H_2 + e \longrightarrow C_2H^+ + H + e$

$C_2H_2 + e \longrightarrow C_2^+ + 2H + e$

$C_4H_2 + e \longrightarrow C_4H_2^+ + 2e$

Ion recombination reactions

$CH^+ + CH_4 \longrightarrow C_2H_4^+ + H$

$CH^+ + CH_4 \longrightarrow C_2H_2^+ + H_2 + H$

$CH_2^+ + CH_4 \longrightarrow C_2H_4^+ + H_2$

$CH_2^+ + CH_4 \longrightarrow C_2H_2^+ + 2H_2$

$CH_2 + CH_4 \longrightarrow CH_3 + CH_3$

$C_2H_4^+ + CH_4 \longrightarrow$ no reaction

$H^+ + {}^\bullet CH \longrightarrow CH^+ + {}^\bullet H$

$H^+ + :CH_2 \longrightarrow CH^+ + H_2$

$C^+ + {}^\bullet CH_3 \longrightarrow C_2H_2^+ + {}^\bullet H$

$CH^+ + {}^\bullet CH \longrightarrow C_2^+ + H_2$

$CH_2^+ + {}^\bullet CH \longrightarrow C_2H_2^+ + {}^\bullet H$

$CH_3^+ + {}^\bullet CH \longrightarrow C_2H_2^+ + H_2$

$C_2H_2^+ + {}^\bullet CH \longrightarrow C_3H_2^+ + {}^\bullet H$

$C_2H_2^+ + :CH_2 \longrightarrow C_3H_3^+ + {}^\bullet H$

$C_2H + H_2 \longrightarrow C_2H_2 + H$

$Cl_2^+ + Cl^- \longrightarrow Cl_2 + Cl$

$Cl^+ + Cl^- \longrightarrow 2Cl$

Neutral recombination reactions

$CH_4 + H \longrightarrow CH_3 + H_2$

$C_2H + C_2H_2 \longrightarrow C_4H_2 + H$

$CH + H_2 \longrightarrow CH_2 + H$

$CH_2 + H \longrightarrow CH + H_2$

$CH_2 + CH_2 \longrightarrow C_2H_2 + 2H$

$CH_2 + H_2 \longrightarrow CH_3 + H$

$CH_2 + CH_3 \longrightarrow C_2H_4 + H$

$C_6H_6 \longrightarrow C_6H_5 + H$

$C_6H_6 + H \longrightarrow C_6H_5 + H_2$

$Cl + Cl + HCl \longrightarrow Cl_2 + HCl$

$H + H + HCl \longrightarrow H_2 + HCl$

$H + Cl + HCl \longrightarrow HCl + HCl$

$Cl + Cl + Cl_2 \longrightarrow Cl_2 + Cl_2$

$H + H + Cl_2 \longrightarrow H_2 + Cl_2$

$H + Cl + Cl_2 \longrightarrow HCl + Cl_2$

$Cl + Cl + H_2 \longrightarrow Cl_2 + H_2$

$H + H + H_2 \longrightarrow H_2 + H_2$

$H + Cl + H_2 \longrightarrow HCl + H_2$

$H + HCl \longrightarrow H_2 + Cl$

$Cl + HCl \longrightarrow Cl_2 + H$

$H + Cl_2 \longrightarrow HCl + Cl$

$Cl + H_2 \longrightarrow HCl + H$

Associative collisional detachment

$Cl^- + H \longrightarrow HCl + e$

Heterogeneous reactions

$CH_3 \longrightarrow CH_3(s) + H_2$

$CH_3^+ \longrightarrow CH_3^+(s) \longrightarrow CH(s) + H_2$

$CH_4^+ \longrightarrow CH_4^+(s) \longrightarrow CH_4$

$CH_5^+ \longrightarrow CH_5^+(s) \longrightarrow CH_4 + H$

$C_2H_4^+ \longrightarrow C_2H_4^+(s) \longrightarrow C_2H_4$

$C_2H_5^+ \longrightarrow C_2H_5^+(s) \longrightarrow C_2H_5$

$CH_3 \longrightarrow CH_3(s) \longrightarrow CH(s) + H_2$

$Cl_{(g)} + 2Cl_{(s)}, H_{(s)} \longrightarrow Cl_{2(s)} + HCl_{(s)}\ ) \longrightarrow Cl_{2(g)} + HCl_{(g)}$

$H_{(g)} + 2Cl_{(s)}, H_{(s)} \longrightarrow H_{2(s)} + HCl_{(s)}\ ) \longrightarrow H_{2(g)} + HCl_{(g)}$

$W—CH_2—Cl + H_{(g)} \longrightarrow W—CH_2\bullet + HCl_{(g)}$

$W—CH_3 + Cl_{(g)} \longrightarrow W—CH_2\bullet + HCl_{(g)}$

$W—CH_2—Cl + H—CH_2—W \longrightarrow W—CH_2—CH_2—W + HCl_{(g)}$

$W—CHCl—CHCl—W \longrightarrow W—CH{=}CCl—W + HCl_{(g)}$

This Matlab code can be divided to 2 parts like shown below.

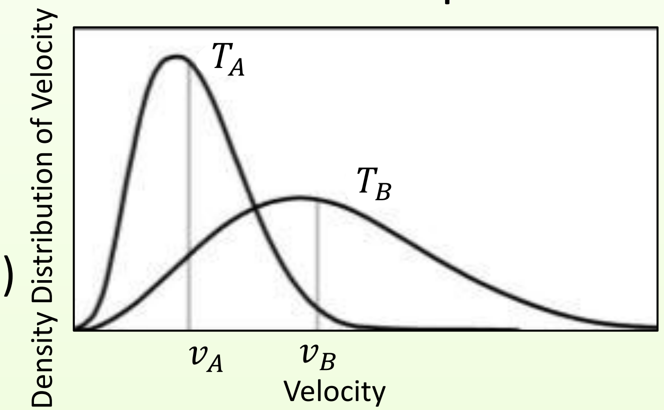
Calculation

Liberman's text book P.98 3.5

Maxwell Boltzman distribution equation

$$K(T) = \langle \sigma(v) v \rangle_V = \int \sigma(v) v \underline{f(v)}\, d^3v$$

$$= \int_0^\infty \sigma(v) v \underline{4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} exp\left(-\frac{mv^2}{2kT}\right)} dv \quad (3.5.2)$$



$$K(T) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty \sigma E exp\left(-\frac{E}{kT}\right) \frac{8mE}{m} \frac{1}{m} dv \qquad \left(\because E = \frac{1}{2} mv^2, dE = mvdv\right)$$

$$K(T_e) = \left(\frac{m}{2\pi T_e q}\right)^{\frac{3}{2}} 8\pi \left(\frac{1}{m}\right)^{\frac{1}{2}} \int_0^\infty \sigma E exp\left(-\frac{E}{T_e q}\right) dv \qquad (\because kT = T_e q)$$

Constant — function

[J/K][K][eV][J/eV]

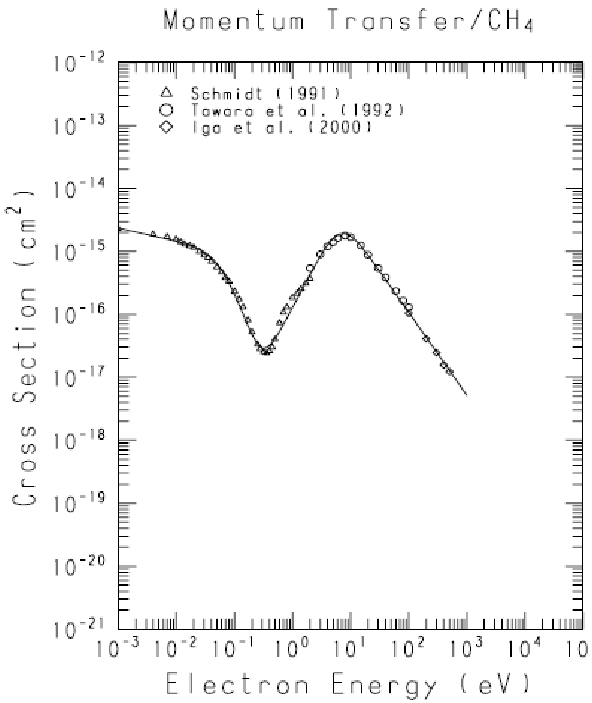
Curve Fitting

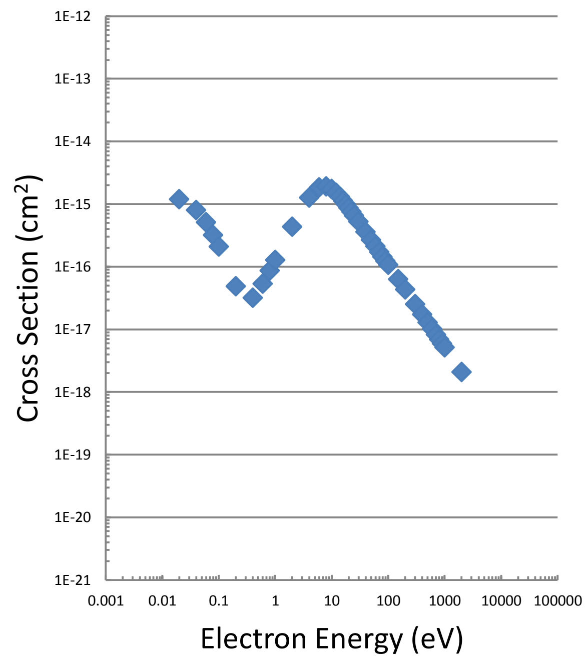
The calculated results are fitted with equation shown below.

$$K(T_e) = aT_e^b exp\left(\frac{c}{T_e}\right)$$

(Fit-Data)/Data⇒0

$$f(\mathrm{E}; c_1, c_2, c_3, c_4, c_5, c_6) = \frac{\sigma_0 c_1 [(E - E_{th})/E_R]^{c_2}}{1 + [(E - E_{th})/c_3]^{c_2 + c_4} + [(E - E_{th})/c_5]^{c_2 + c_6}}$$





E[eV]	Cross secton [cm^2]
0.1	2.08224×10^{-16}
0.2	4.82733×10^{-17}
0.4	3.17070×10^{-17}
0.6	5.34728×10^{-17}
0.8	8.64750×10^{-17}
1	1.27660×10^{-16}
2	4.30073×10^{-16}
4	1.26317×10^{-15}
6	1.82695×10^{-15}
8	1.90500×10^{-15}
10	1.73384×10^{-15}
12	1.50776×10^{-15}
14	1.29921×10^{-15}
16	1.12422×10^{-15}
18	9.81177×10^{-16}
20	8.64522×10^{-16}
30	5.18484×10^{-16}
40	3.56822×10^{-16}
60	2.09677×10^{-16}
80	1.43602×10^{-16}
100	1.07036×10^{-16}
200	4.29395×10^{-17}
400	1.72230×10^{-17}
600	1.00930×10^{-17}
800	6.90801×10^{-18}
1000	5.14785×10^{-18}

Robert/David's Matlab Code

[2] T. SHIRAI, T. TABATA, H. TAWARA, Y. ITIKAWA, "ANALYTIC CROSS SECTIONS FOR ELECTRON COLLISIONS WITH HYDROCARBONS: CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, AND C_3H_6", Atomic Data and Nuclear Data Tables **80**, (2002)

4. Results

The rate constant coefficients were shown below. $k_v = aT_e^b exp\left(-\frac{c}{T_e}\right)$

Reaction	A	B	C
CH_4+e ⇒ CH_4+e	4.136×10^{-13}	0.031	2.512
CH_4+e ⇒ CH_4^++2e	2.379×10^{-14}	0.388	14.255
CH_4+e ⇒ CH_3^++H+2e	1.864×10^{-14}	0.402	15.725
CH_4+e ⇒ CH_2^++H_2+2e	4.331×10^{-16}	1.166	16.185
CH_4+e ⇒ CH^++H_2+H+2e	9.950×10^{-16}	0.723	24.305
C_2H_2+e ⇒ C_2H_2+e	5.860×10^{-13}	-0.158	3.788
C_2H_2+e ⇒ $C_2H_2^+$+2e	2.594×10^{-14}	0.618	13.583
C_2H_2+e ⇒ C_2H^++H+2e	8.387×10^{-15}	0.504	18.485
C_2H_2+e ⇒ C_2^++2H+2e	1.301×10^{-15}	0.739	21.759
C_2H_2+e ⇒ CH^++CH+2e	1.309×10^{-15}	0.857	23.032

CF_4+e ⇒ CF_4+e	A	B	C
Reference	7.14×10^{-14}	0.451	0.351
From this model	6.96×10^{-14}	0.680	0.723

[1] G Kokkoris, A Goodyear, M Cooke and E Gogolides, ”Global Model for C4F8 Plasma Coupling Gas Phase & Wall Surface Reaction Kinetices”, J. Phys. D: Appl. Phys. **41**, 195211 (2008)

<u>The results has good correlation with reference data.</u>

4. Results

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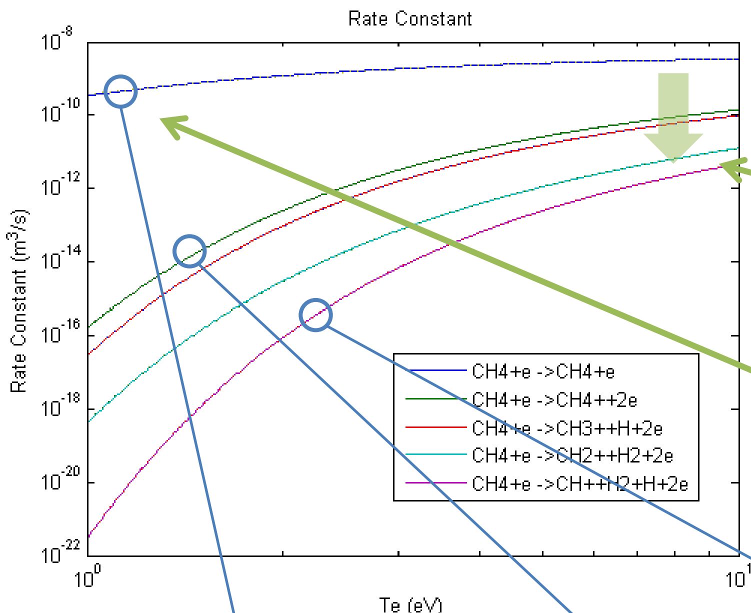
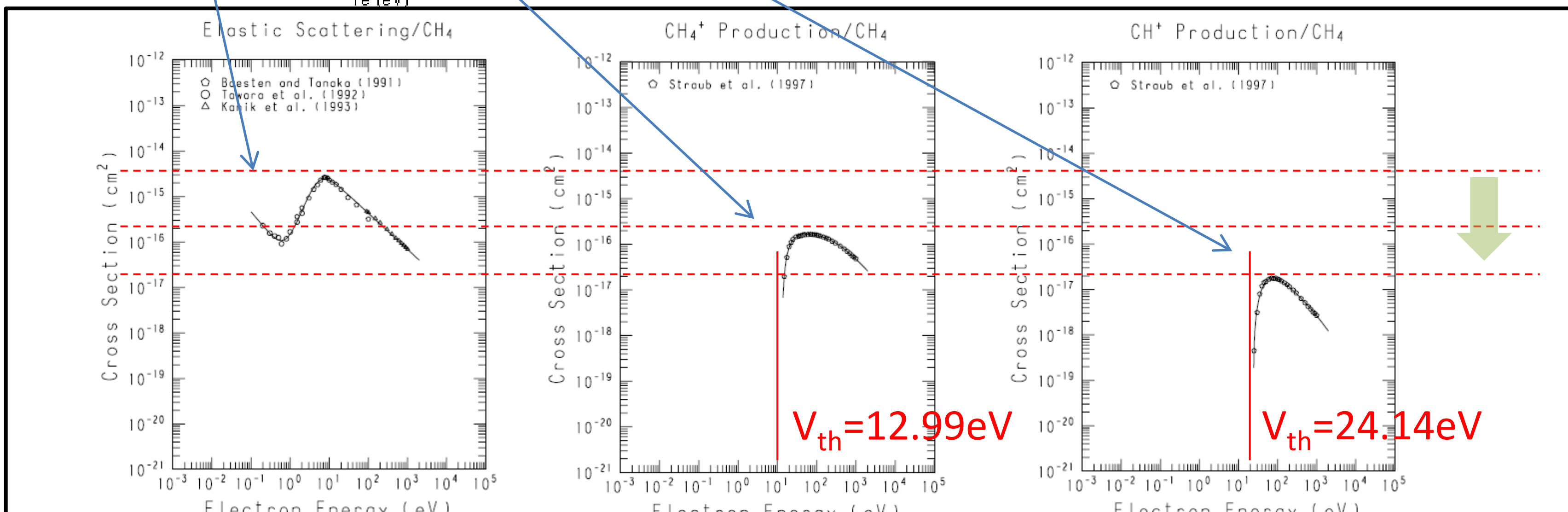
Nagoya University



Rate constant magnitude affected by cross sectional data

In Elastic collision, the value doesn't decrease dramatically because the threshold energy doesn't exist



[2] T. SHIRAI, T. TABATA, H. TAWARA, Y. ITIKAWA, "ANALYTIC CROSS SECTIONS FOR ELECTRON COLLISIONS WITH HYDROCARBONS: CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, AND C_3H_6", Atomic Data and Nuclear Data Tables **80**, (2002)

5. Conclusion

Hori・Sekine Lab. Nagoya University

・We established rate coefficient calculation system from cross sectional data.

・More results are needed for the simulation Global Model for C_8H_9Cl Plasma Coupling Gas Phase & Wall Surface Reaction Kinetics.

6. Future work

・The others rate constant will be calculated with the cross sectional data from the papers obtained already.

・Cross sectional data will be measured with OES e-beam equipment to get constant rates for all reactions.

Elastic collisions

$$2ClpX + e \longrightarrow 2ClpX + e$$

Vibrational excitation

$$2ClpX + e \longrightarrow 2ClpX(v) + e$$

Dissociation reactions

$$2ClpX + e \longrightarrow \bullet pX + \bullet Cl$$

$$2ClpX + e \longrightarrow \bullet ClT + \bullet CH_3$$

$$2ClpX + e \longrightarrow 3\bullet C_2H + 2\bullet CH_3 + \bullet Cl$$