Basic 11
High Knudsen Number Flows

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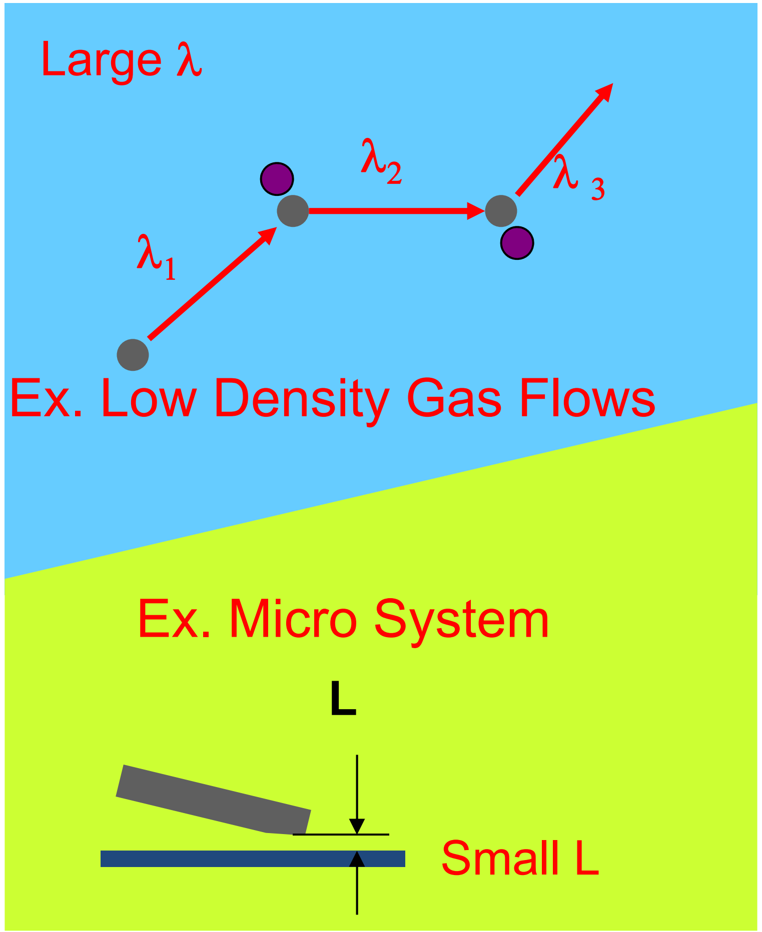
High Knudsen Number Flows



Knudsen number

$Kn=\lambda/L$

λ : Mean Free Path

L : Characteristic Dimension

Continuum approach invalid

Kn larger than ~0.1

→ " High *Kn* Number Flow "

(Large λ **or** Small L)

Flow field is strongly influenced by interaction of molecules with a solid boundary rather than intermolecular collisions

Mean Free Path

Mean Free Path

Average distance that a molecule travels between successive collisions

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$$

d : diameter of a molecule
n : number density

Loschmit’s Number

The molecular number density of an ideal gas at standard condition [0°C, 1 atm(=760 Torr =760 mmHg)] in 1 cm^3

$n = 2.68699 \times 10^{19}\ \mathrm{cm}^{-3}$

Mean free path in atmospheric pressure condition

Air: single molecular gas, mean diameter of a molecule $d = 3.7 \times 10^{-10}$ m

→ $\lambda = 6.1 \times 10^{-8}$ m (61 nm)

From the equation of state $p = nkT$ → $\lambda \propto T/p$

(p: pressure, T: Temp., k:*Boltzmann*’s const.)

→ λ is inversely proportional to P and proportional to T

Traditional High Knudsen Number Flow

Rarefied Gas Flow or Atomic/Molecular Gas Flow

Rarefied Gas Flow
Atomic/Molecular Gas Flow

- Continuum Approach invalid
  - Analyses by Boltzmann Eq.
  - Direct Simulation Monte Carlo (DSMC)
- Nonequilibrium Phenomena
- Strong Influence of Interface
  - Accommodation Coefficient
  - Adsorption Probability
  - Physical Models of Solid Surface

International Symposium on Rarefied Gas Dynamics (since 1958)

Rarefied Gas Dynamics (RGD) has developed along with space technologies from 1950's and expanded into analyses of low density gas flows in vacuum technologies (such as semiconductor film growth)

From Rarefied Gas Flow to High Knudsen Number Flow

In so-called nano-technologies, attention has been focused mainly on fabrication of devices, but not on gas-surface interaction which is important for the devices working in ambient gas.

Flows around the micro-devices are also in the category of "Rarefied gas flows", but it is difficult to accept that because the devices work mainly in the atmospheric condition

↓

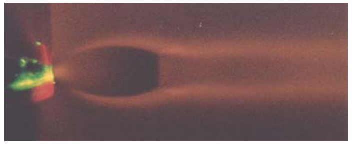
"High Knudsen Number Flow"

High Knudsen Number Flows

Technologies related to
Ultra-High Vacuum
Mean Free Path λ: large

High Kn Number Flows

Nano- and Micro-Devices
Characteristic Dimension
L: small

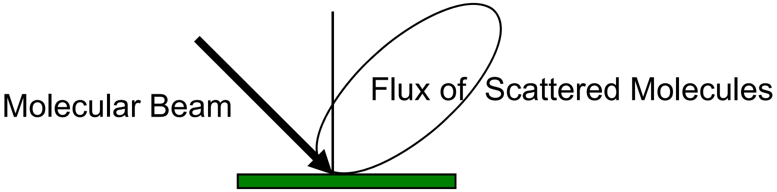


Strongly Nonequilibrium Gas Flows

Small Number of
Intermolecular Collisions

Flow field is strongly influenced
by interaction of molecules
with a solid boundary

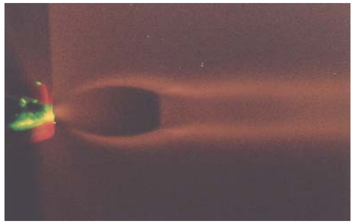
Gas-Surface Interaction

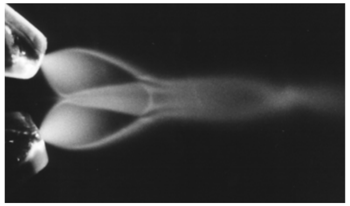


Lack of Precise
Experimental Data

High Knudsen Number Flows Challenge of Our Group

Analyses of Flow Filed Structures and Nonequilibrium Phenomena of the Low Density Gas Flows





Developments of Measurement Techniques using interaction of Laser Beams with Molecules

Measurement Techniques in Molecular Level:

LIF, CARS, DFWM, REMPI

Database Creation for Gas-Surface Interaction

Momentum and Energy Accommodation Coefficients

Experiments using a Molecular Beam and Detection of Reflected Gas Molecules including Internal Energy by use of REMPI

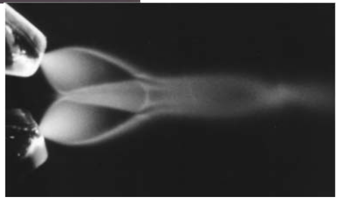
Pressure Distribution on Solid Surfaces in High Knudsen Number Flows

We can not Apply Pressure Taps to the Low Density Gas Flows and Micro- and Nano-Systems

→ **Development of Measurement Techniques in Molecular Level**

: PSMF (Pressure Sensitive Molecular Film)

Development of Optical Diagnostic Methods
for High Knudsen Number Flows



LIF

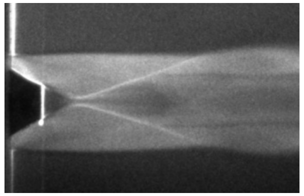
Laser Induced Fluorescence : I_2, O_2 and NO

Flow visualization

Fujimotto, Niimi, Rarefied Gas Dynamics, AIAA(1988), 391-406

Niimi; Protokoll des DLR-Kolloquiums LIF-8, (1996), 62-68

Mori, Niimi, et al; AIAA paper 2005-1350, AIAA, 2005-01(USA, Reno)



Temperature measurement technique

Niimi, et al; OPTICS LETTERS, 15-16(1990) , 918-920

Niimi, et al; Applied Optics, 34, 27(1995), 6275-6281

CARS

Coherent Anti-Stokes Raman Scattering : N_2

DFWM

Degenerate Four Wave Mixing : I_2

REMPI

Resonantly Enhanced Multi-Photon Ionization : N_2

Mori, Niimi, et al; Physics of Fluids, 17, 117103(2005)

Development of Optical Diagnostic Methods
for High Knudsen Number Flows

LIF

Laser Induced Fluorescence of I_2

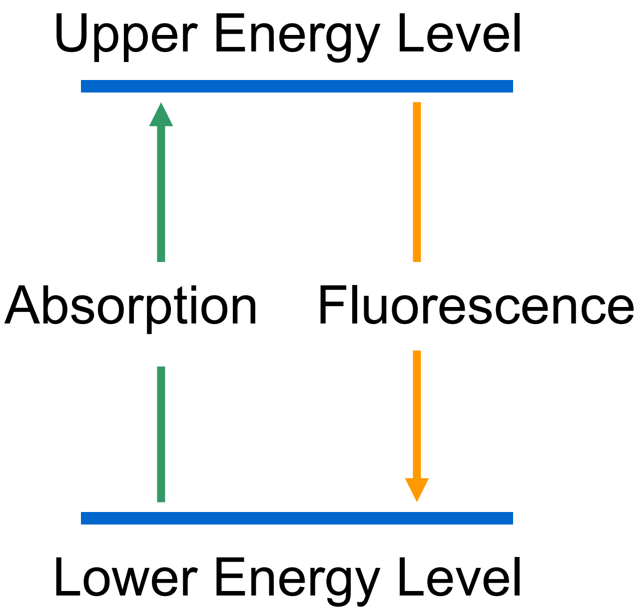
- Flow visualization of interacting supersonic free jets
- Rotational temperature measurement technique

REMPI

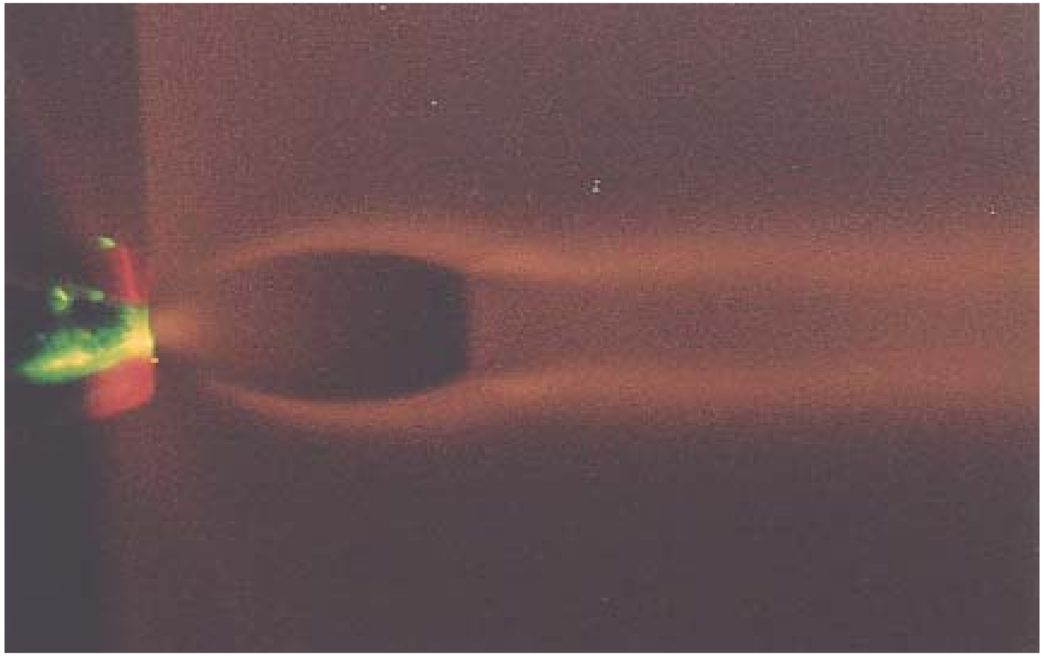
Resonantly Enhanced Multi-Photon Ionization : N_2

- Application of REMPI to highly rarefied gas flows
- Rotational nonequilibrium (non-Boltzmann distribution)

Laser Induced Fluorescence



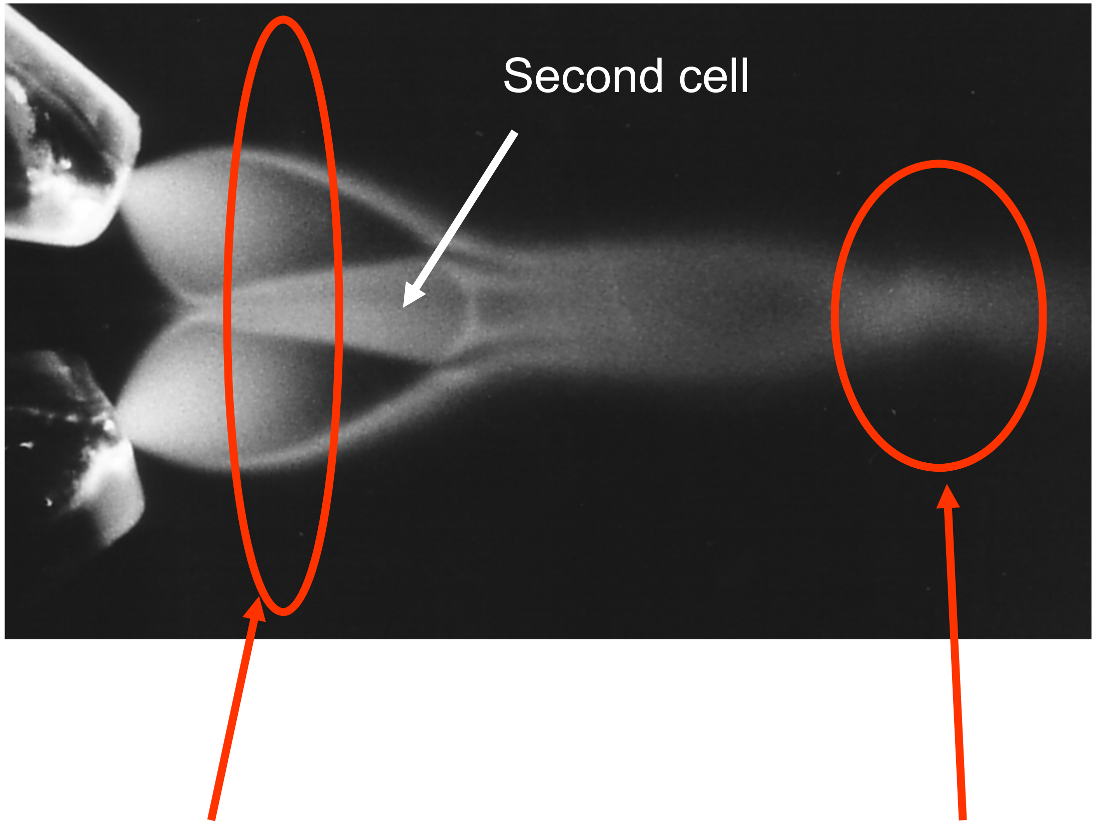
Principle of LIF



A supersonic Ar-free jet visualized by I_2-LIF
Nozzle Diameter: 0.5 mm
Ps/Pb= 150

Application of I_2-LIF to Flow Visualization

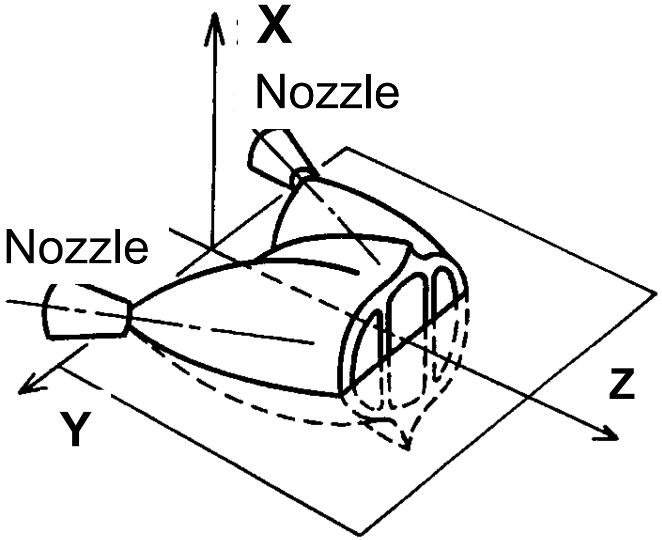
Flow field structure of two interacting supersonic free jets



ϕ-shaped structure

planar flow

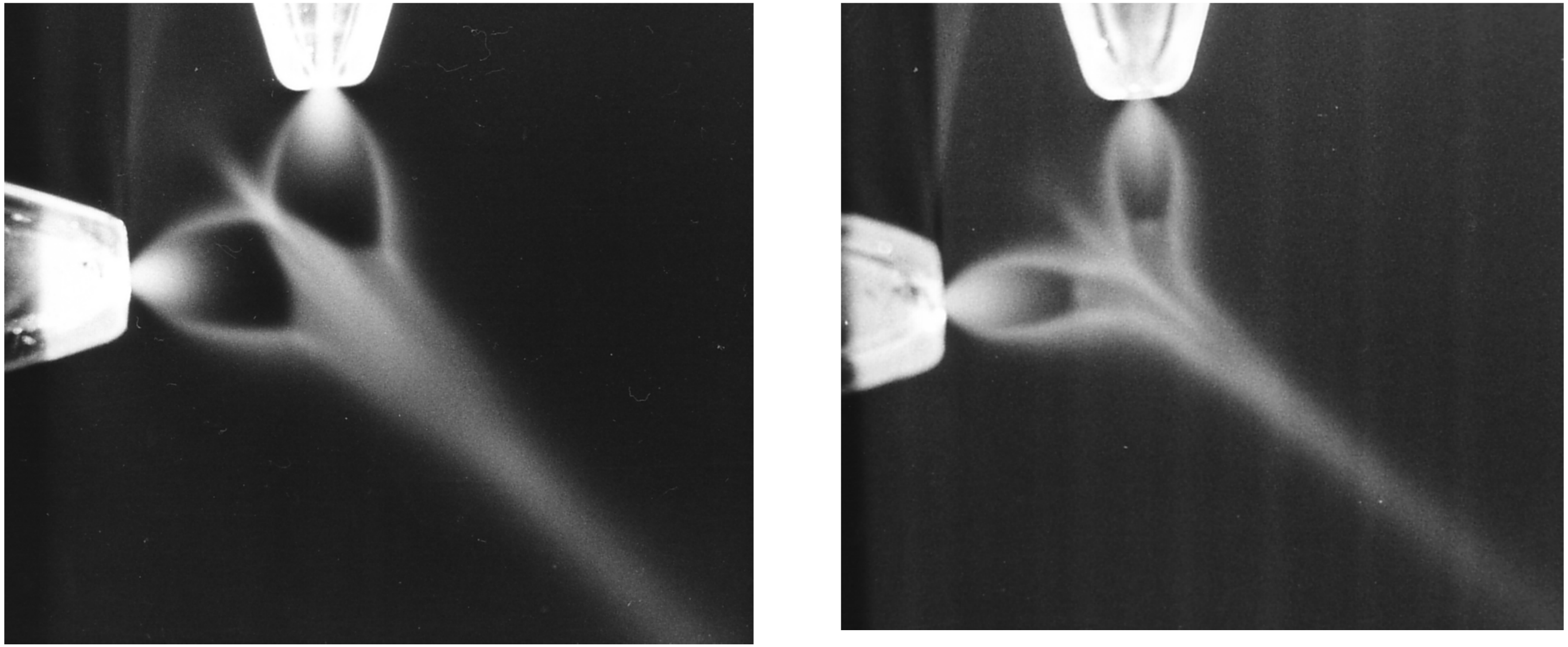
θ=45 deg



Application of I_2-LIF to Flow Visualization

Flow field structure of two interacting supersonic free jets

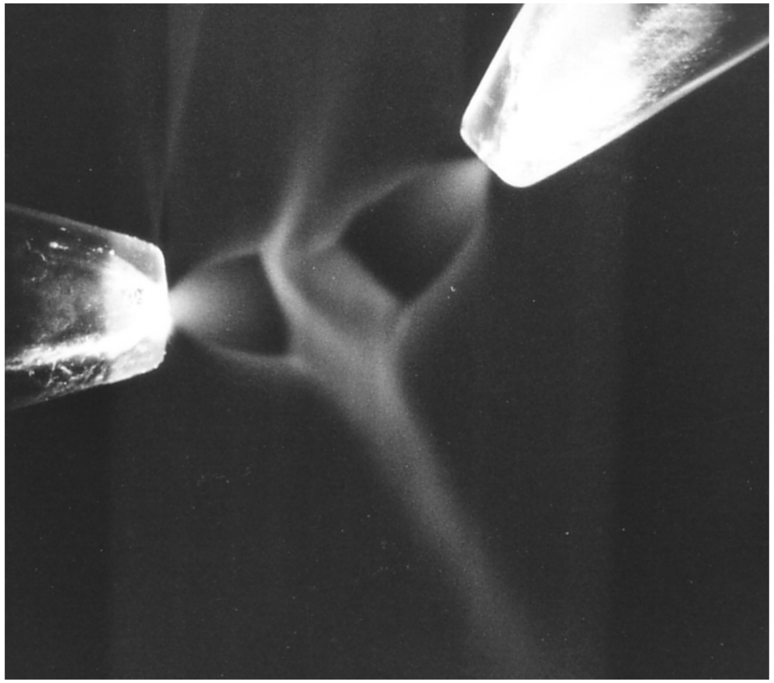
θ=90 deg



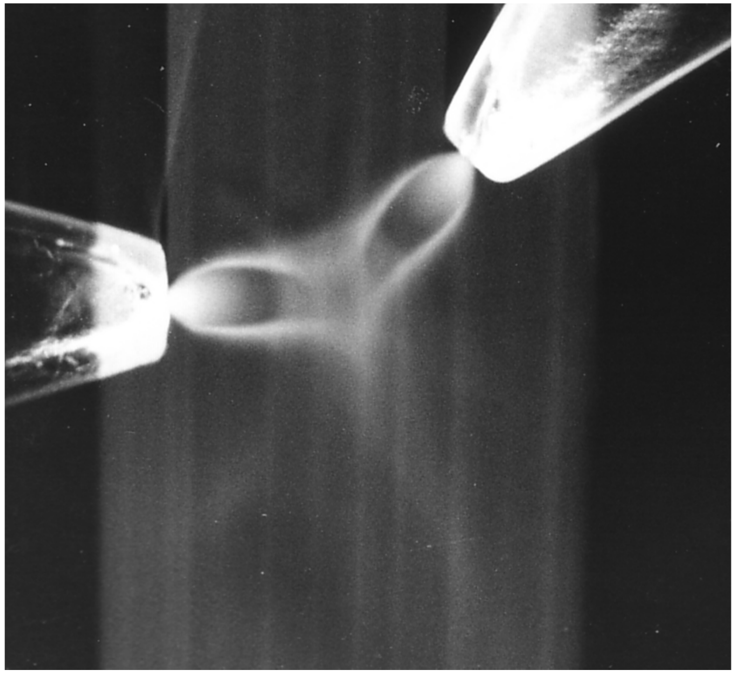
Application of I$_2$-LIF to Flow Visualization

Flow field structure of two interacting supersonic free jets

θ=135 deg



stable

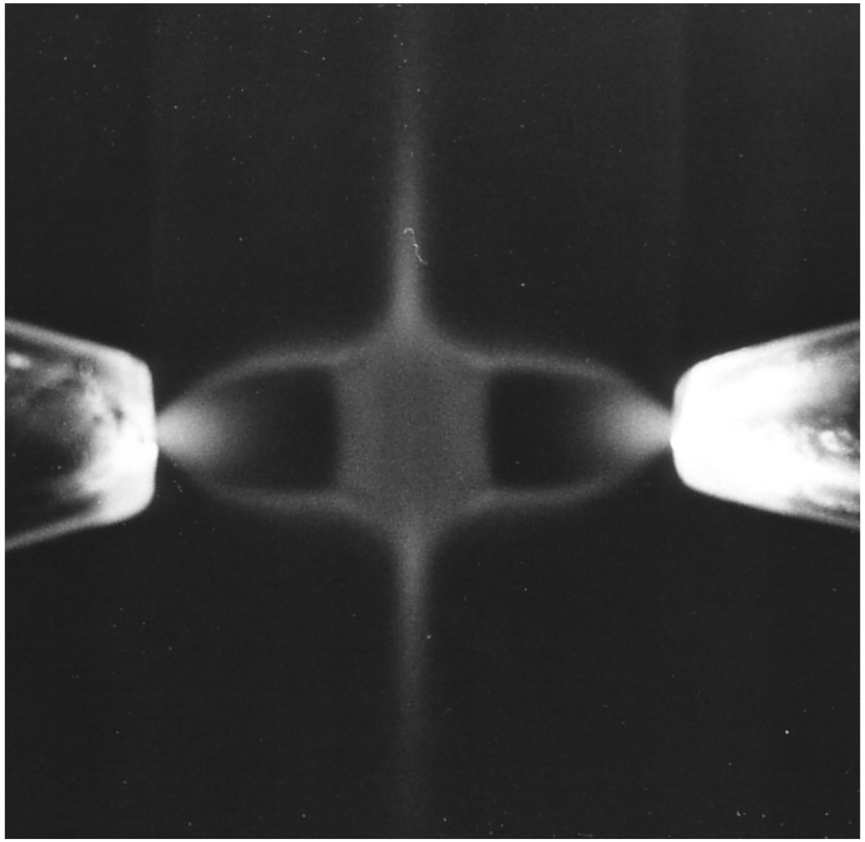


unstable

Application of I_2-LIF to Flow Visualization

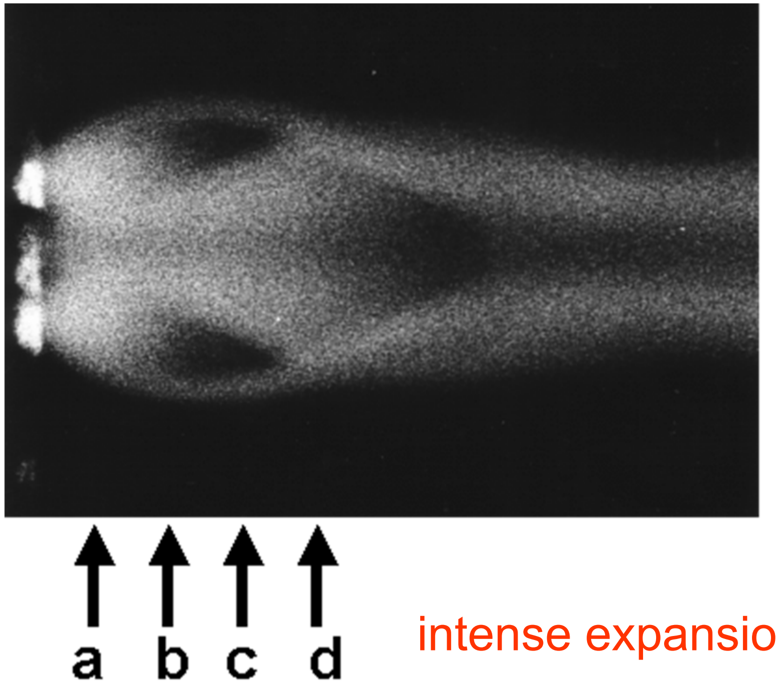
Flow field structure of two interacting supersonic free jets

θ=180 deg



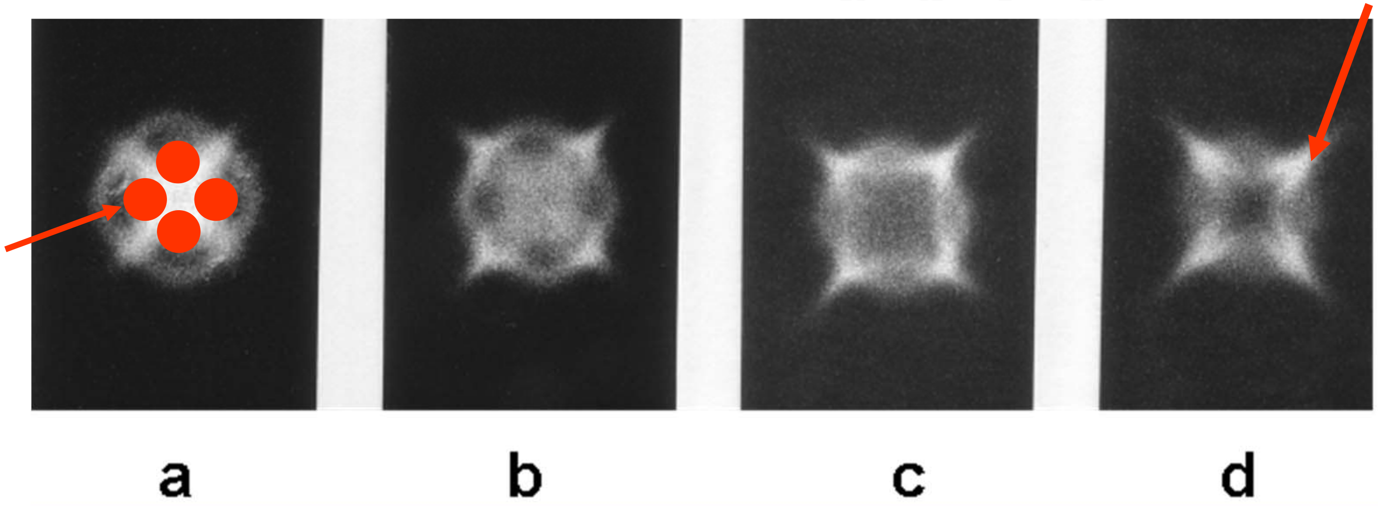
Application of I_2-LIF to Flow Visualization

Flow field structure of
four interacting parallel
supersonic free jets



square arrangement of orifices

intense expansion



orifice

Rotational Temperature Measurement using LIF

Fluorescence intensity F (Two-Level Model)

$$F= C[A_{ji}/(A_{ji}+Q)]B_{ij}IfN_{I2}$$

C :a constant, A_{ji} : spontaneous emission rate,
B_{ij} : stimulated-emission rate, Q : collision quenching rate,
I : intensity of laser beam, N_{I2} : number density of I_2,
f : fraction of the ground-state population

Fluorescence intensity F_1 when the I_2 molecules in the rot. level J''_1 are excited
F_2 when the I_2 molecules in the rot. level J''_2 are excited
a ratio between these two fluorescence intensities

$$F_1/F_2=[(B_{ij})_1 f_1]/[(B_{ij})_2 f_2],$$

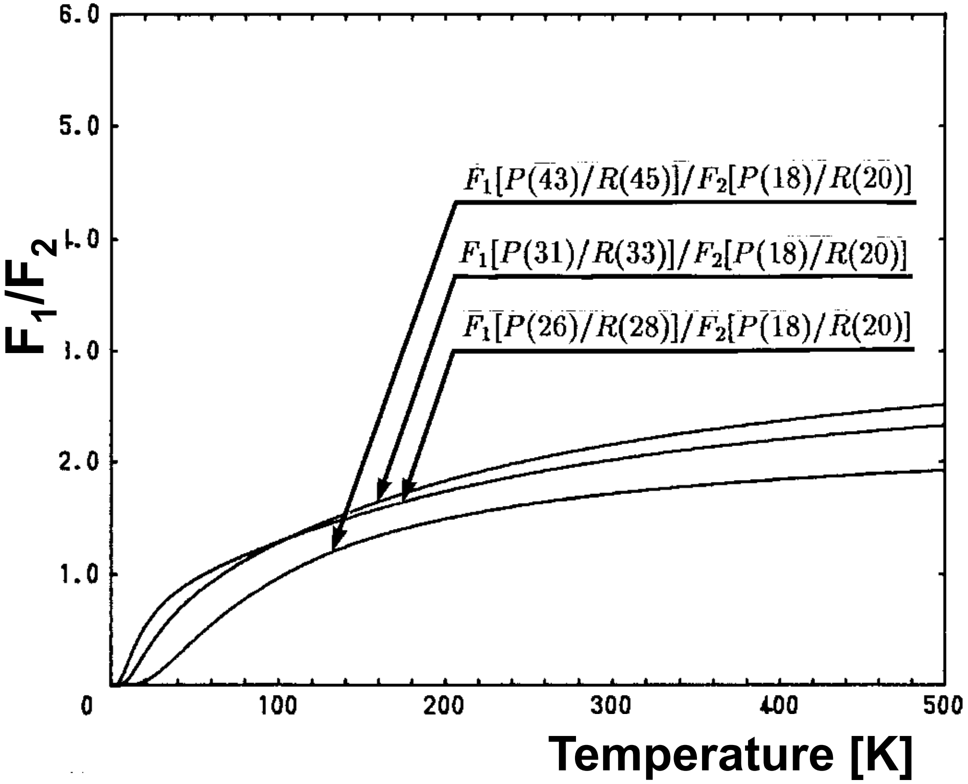
If using common electronic and viblational state for F_1 and F_2,

$$F_1/F_2=[S(J''_1)f_r(J''_1,T)]/[\ S(J''_2)f_r(J''_2,T)]$$

S : Honl-London factor, fr : fraction of the rotational population

Once two lines are selected, the ratio can be expressed as a function of temp.

F_1/F_2 - Temperature



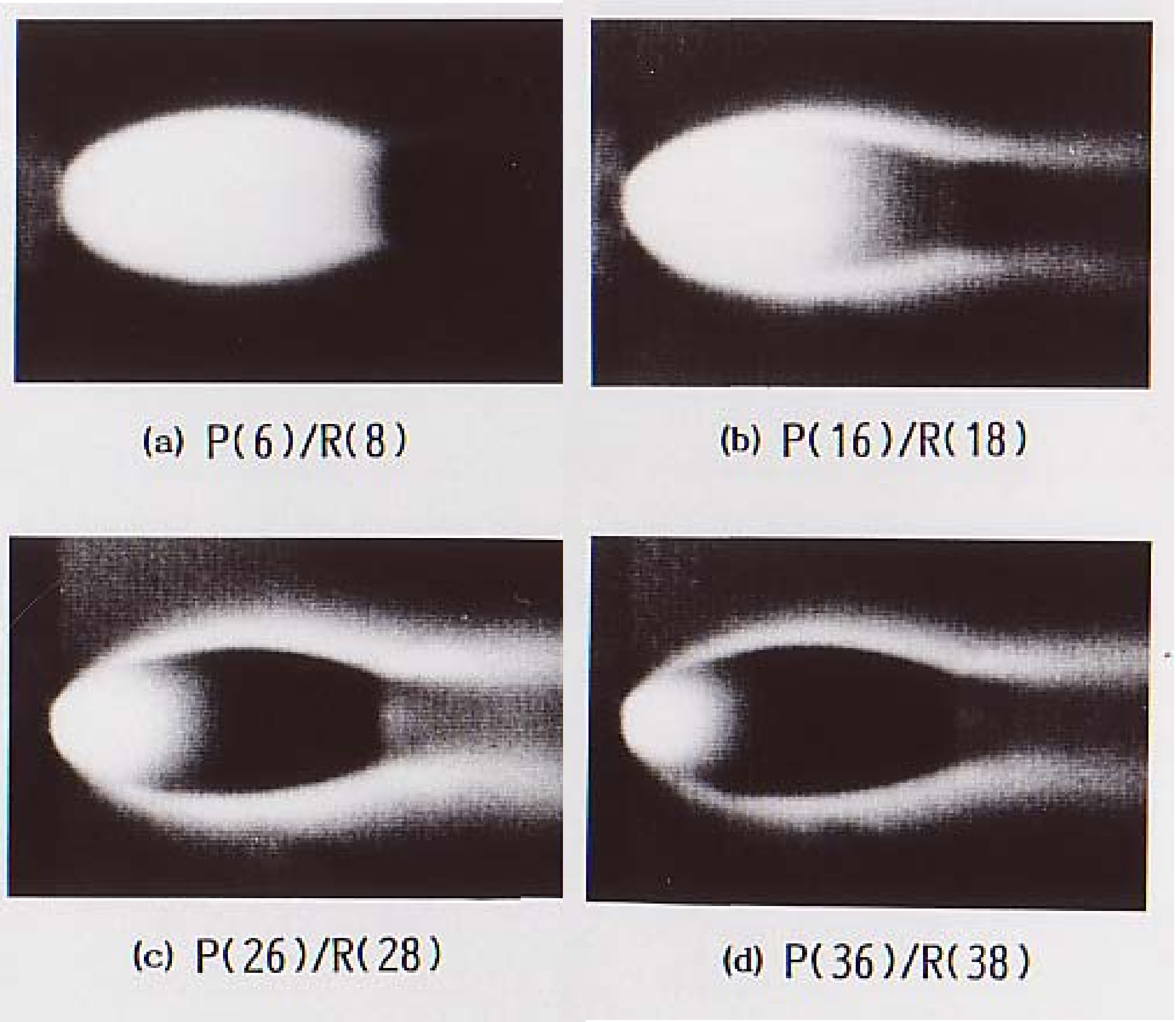
Absorption lines of I_2 molecules in the transition of

$$B\,{}^3\Pi_{ou}^{+}\ (v'=43) \leftarrow X\,{}^1\Sigma_g^{+}\ (v''=0)$$

Wave Number	Absorption Line
19432.0415	*P*(8)/*R*(10)
28.0283	*P*(16)/*R*(18)
26.6531	*P*(18)/*R*(20)
19.6717	*P*(26)/*R*(28)
14.0906	*P*(31)/*R*(33)
396.8701	*P*(43)/*R*(45)

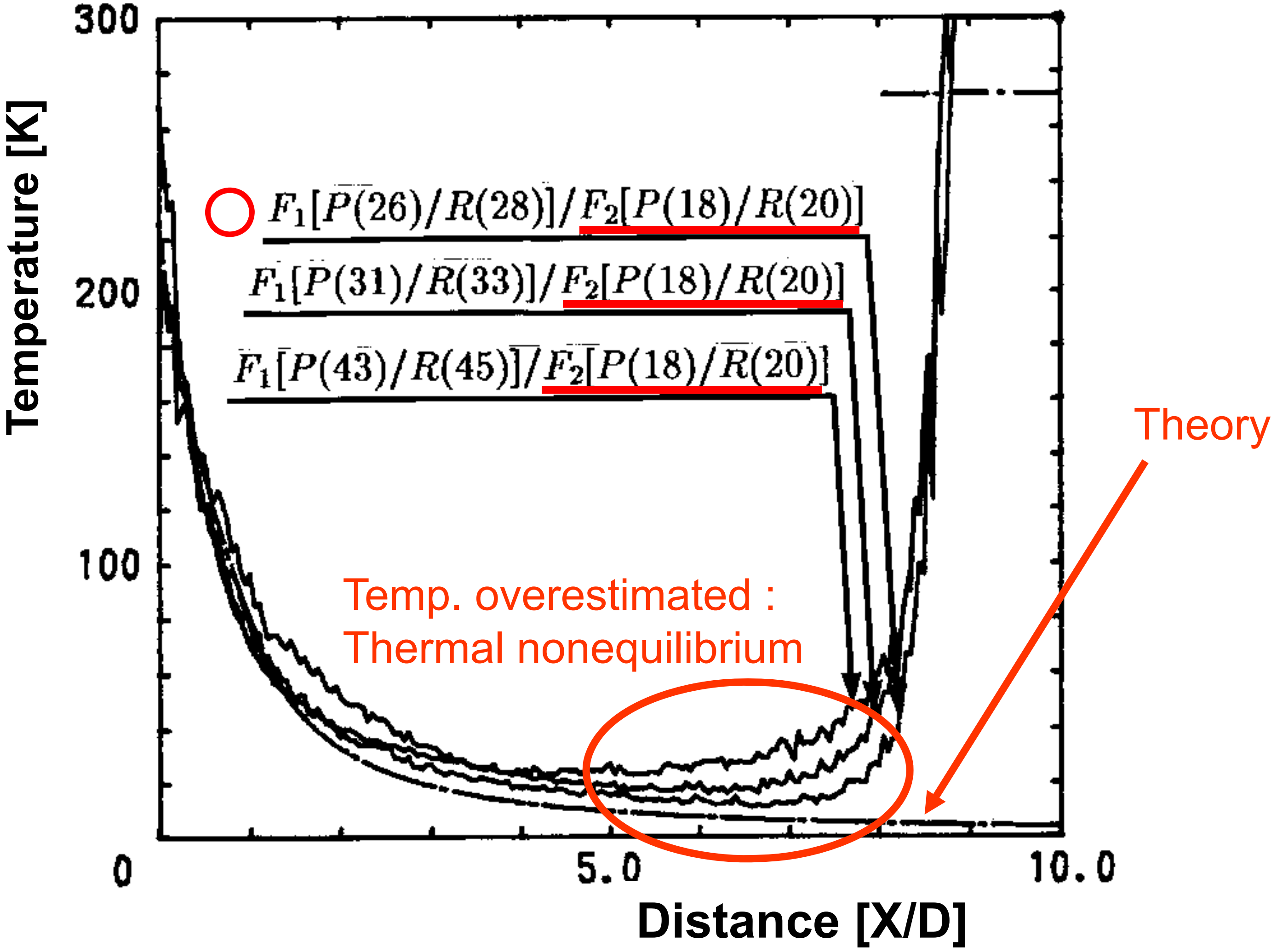
Fluorescence Intensity distribution depending on absorption lines

Supersonic free jets visualized by the use of irradiation of laser beams at wavelengths corresponding to the absorption lines



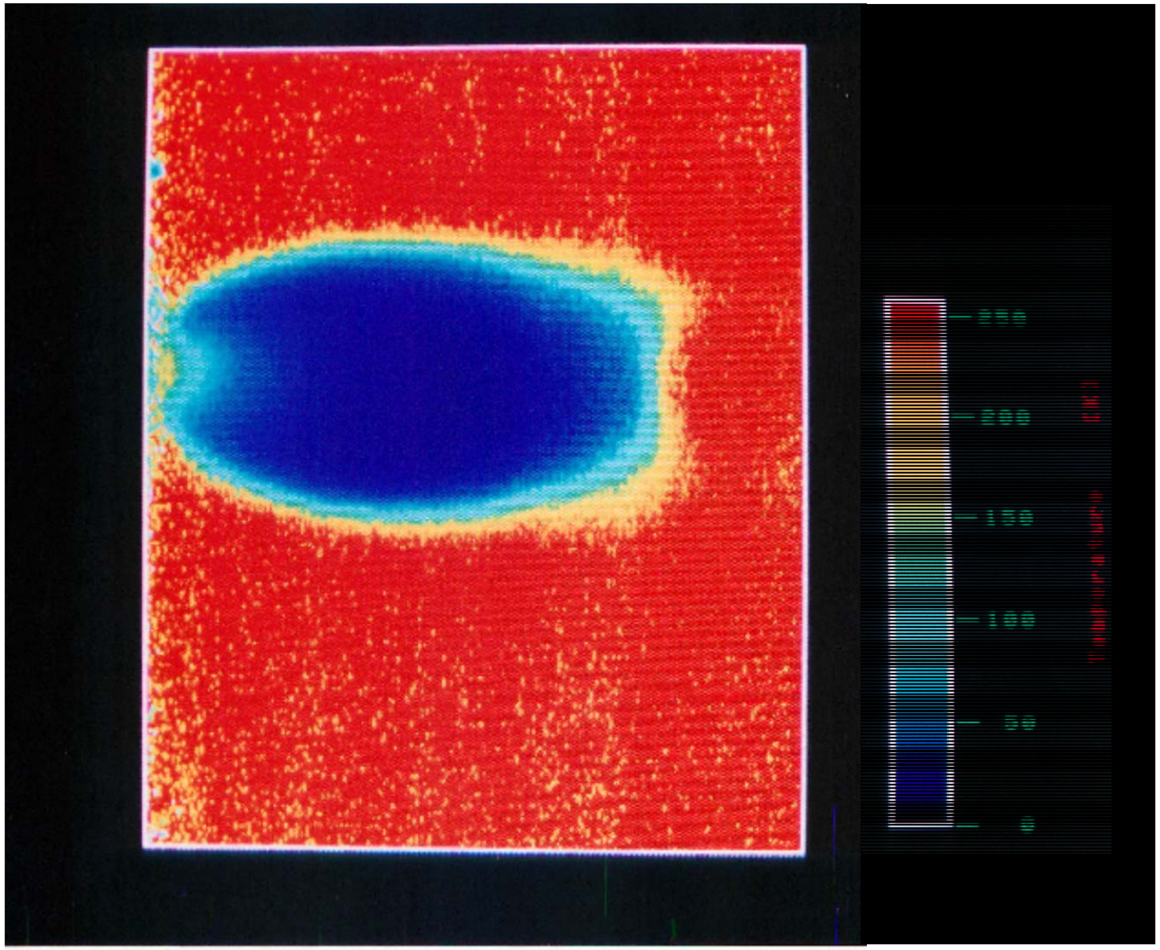
P_s=16 kPa
P_b=100 Pa

Rotational Temperature distribution along the centerline of a Supersonic Free Jet



Temp. overestimated : Thermal nonequilibrium

Rotational Temperature Distribution of a Supersonic Free Jet

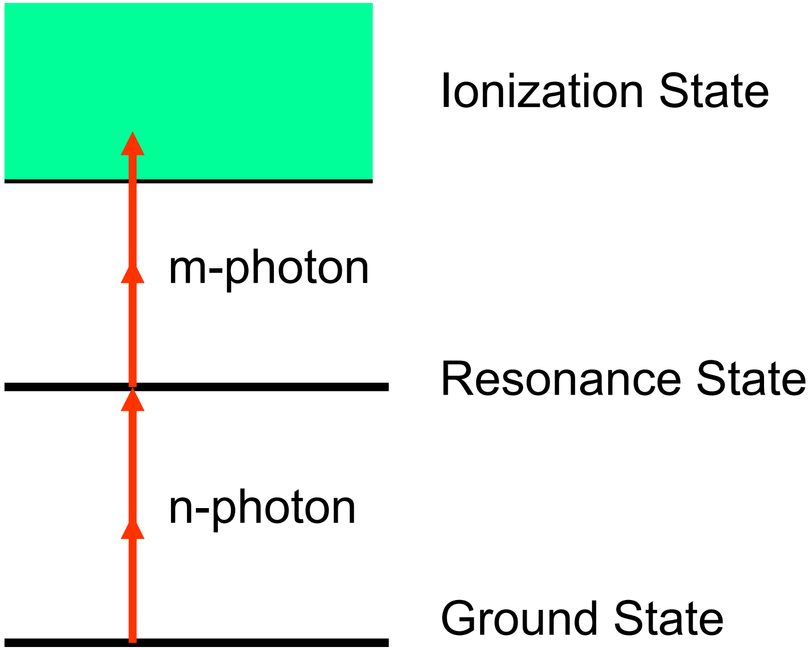


T. Niimi, et al, ***Optics Letters***, 15-16(1990), 918-920
T. Niimi, et al, ***Applied Optics***, 34, 27(1995), 6275-6281

REMPI

Resonantly Enhanced Multi-Photon Ionization

Non-intrusive Measurement Technique with High Sensitivity and Short Response,
allowing measurement of non-equilibrium phenomena in the highly rarefied gas flows



Ionization State

m-photon

Resonance State

n-photon

Ground State

nR+m REMPI Process

Multi-Photon Ionization（MPI)
Low Ionization Rate
(by 1 step)

REMPI
High Ionization Rate
(by 2 steps)

- Short Response
- High Sensitivity
  for $2R+2N_2$-REMPI
  10^9 molecules/cm^3

Objective of Our Study

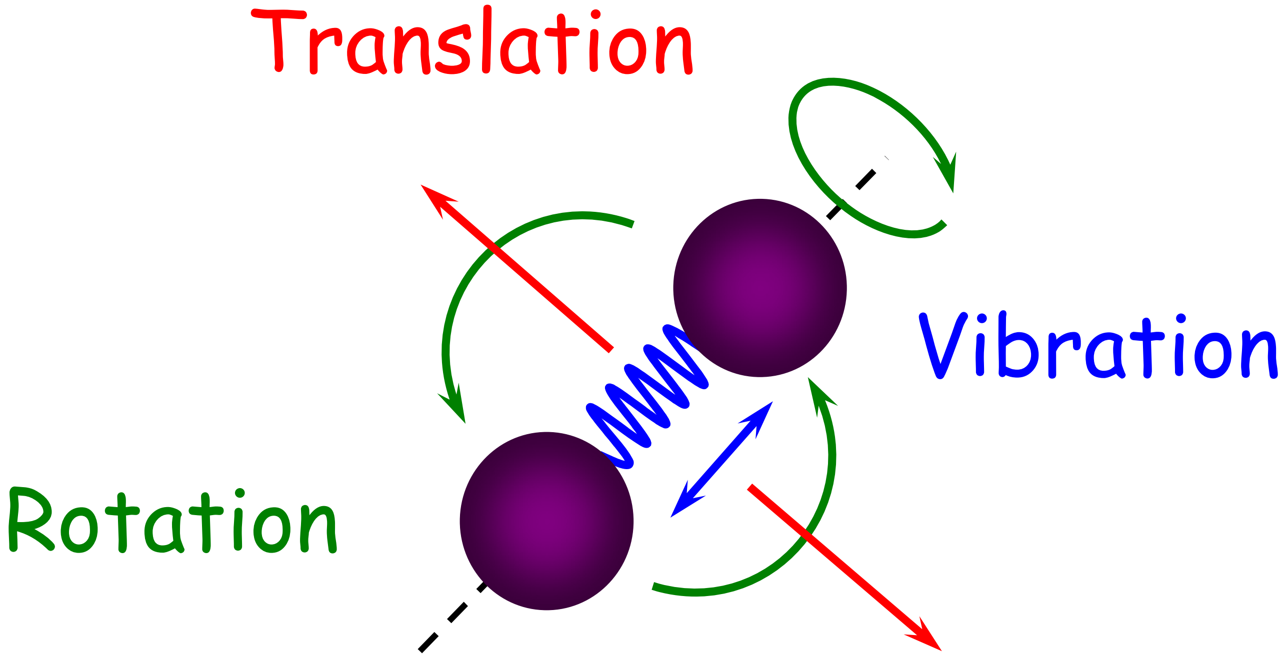
Experimental detection of the non-Boltzmann distribution of the rotational levels (strongly nonequilibrium), applying the REMPI (Resonantly Enhanced Multi-Photon Ionization) method to the supersonic nitrogen free jets with P_0D of 15 Torr-mm or lower.

P_0D: Parameter depending inversely on nozzle Knudsen number

P_0 : stagnation pressure

D : orifice diameter

Modes of Motion for Diatomic Molecule



Distributions for translational and rotational energies

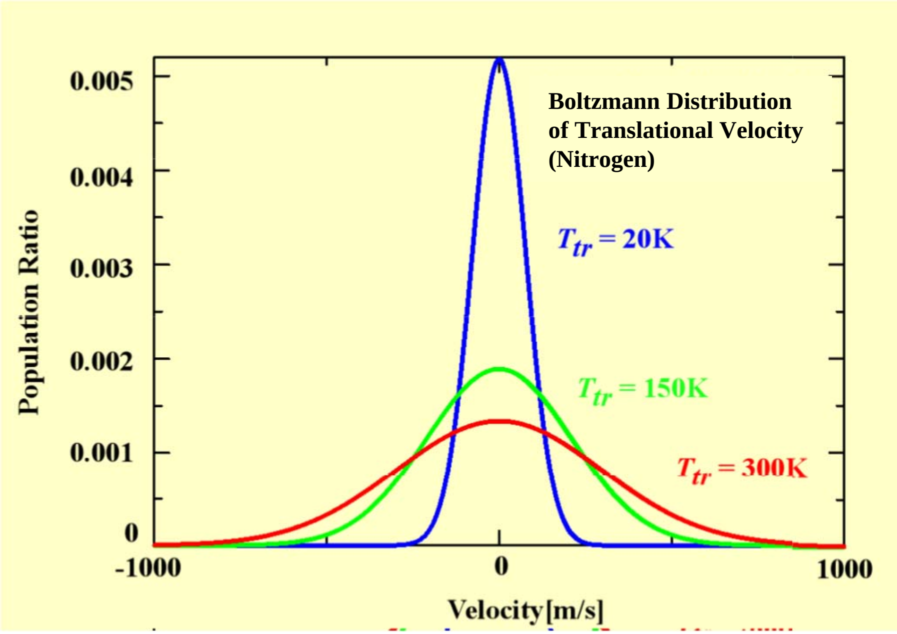
Boltzmann distributions (thermodynamic equilibrium)

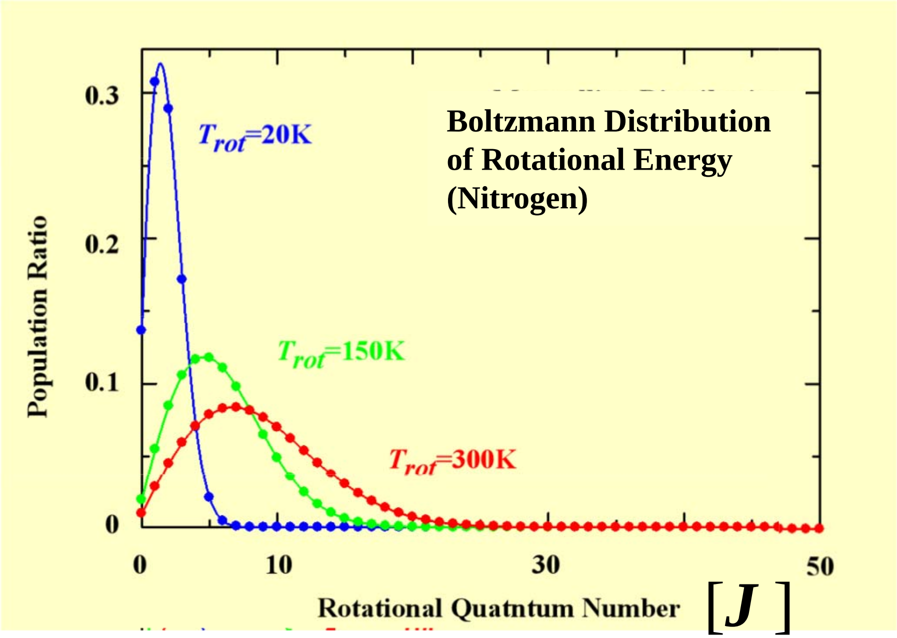
Translational Velocity

$$f(C_x)=\left(\frac{m}{2\pi kT_{tr}}\right)^{\frac{1}{2}}\exp\left(-\frac{mC_x^{\,2}}{2kT_{tr}}\right)$$

Rotational energy

$$N(J)\propto(2J+1)\exp\left(-\frac{E_{rot}}{kT_{rot}}\right)$$





T_{tr}: Translational temp.

T_{rot}: Rotational temp.

Temperature is a determining factor of these distributions

2R+2 N_2-REMPI

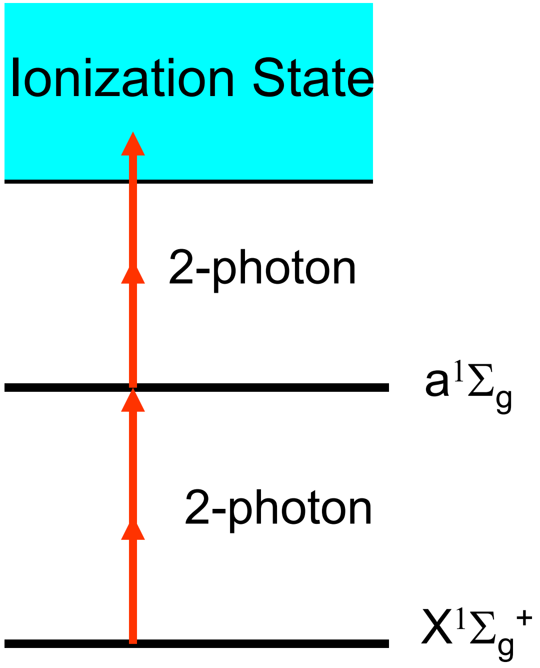
Resonantly Enhanced Multi-Photon Ionization

Non-intrusive Measurement Technique with High Sensitivity and Short Response, allowing measurement of non-equilibrium phenomena in the highly rarefied gas flows

Rotational Line Intensity

$$I_{J',J''} = C g(J'') S(J',J'') \exp(-E_{rot}/kT_{rot})$$

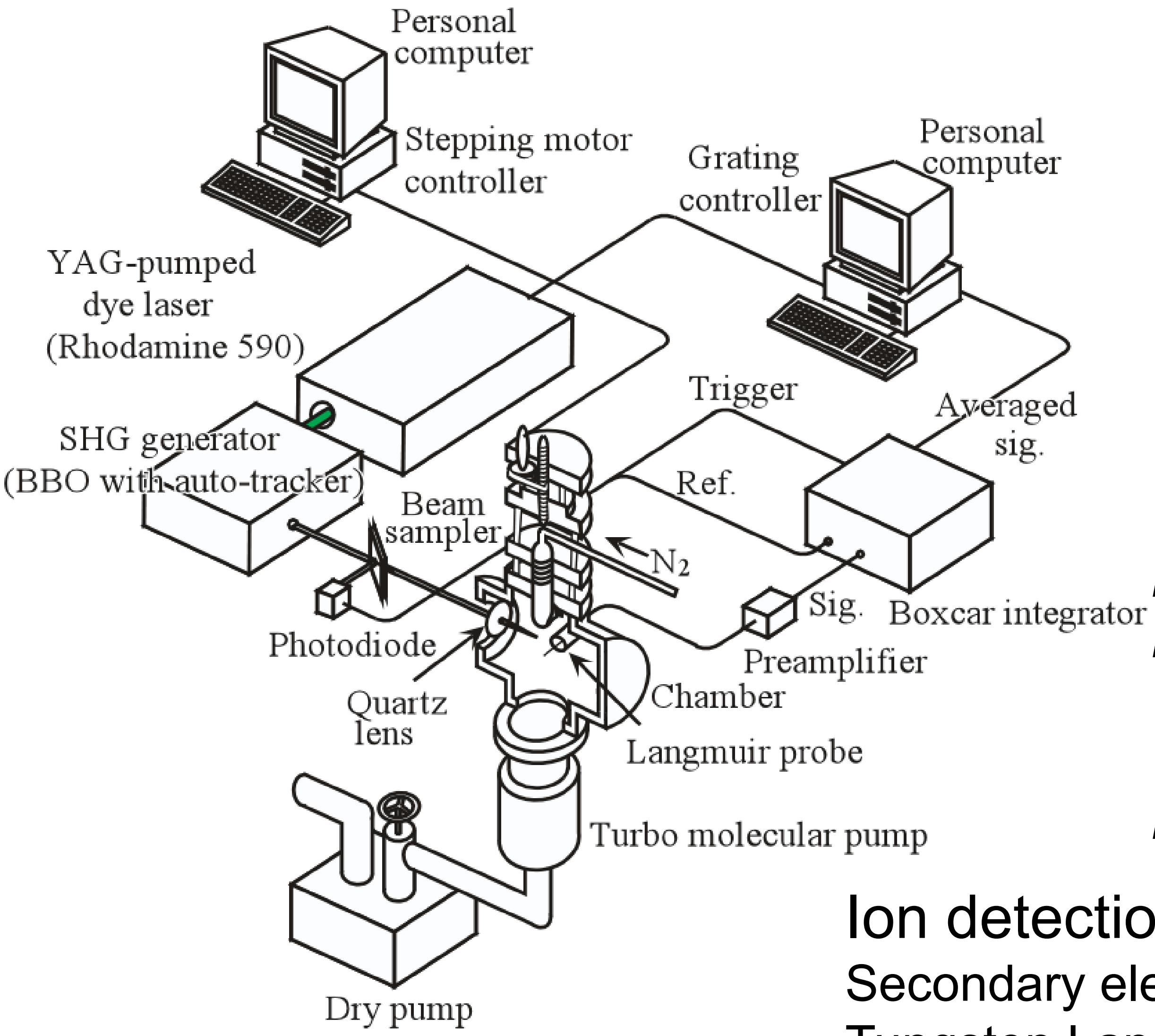
C: constant
$g(J'')$: nuclear spin degeneracy
$S(J',J'')$:2-photon Hönl-London factor
E_{rot} : rotational energy
k : Boltzmann's constant
T_{rot} : rotational temperature

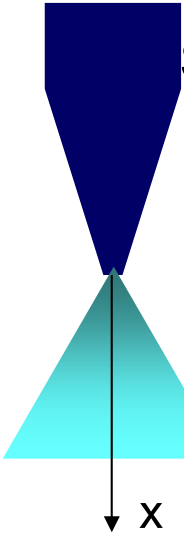


2R+2 N_2 REMPI Process

Photon energy is reduced to one-fourth of EBF
The ejected electrons by photons excite no other molecules or ions again
No consideration of the secondary electrons

Experimental Apparatus





Sonic
Nozzle
D=0.5mm

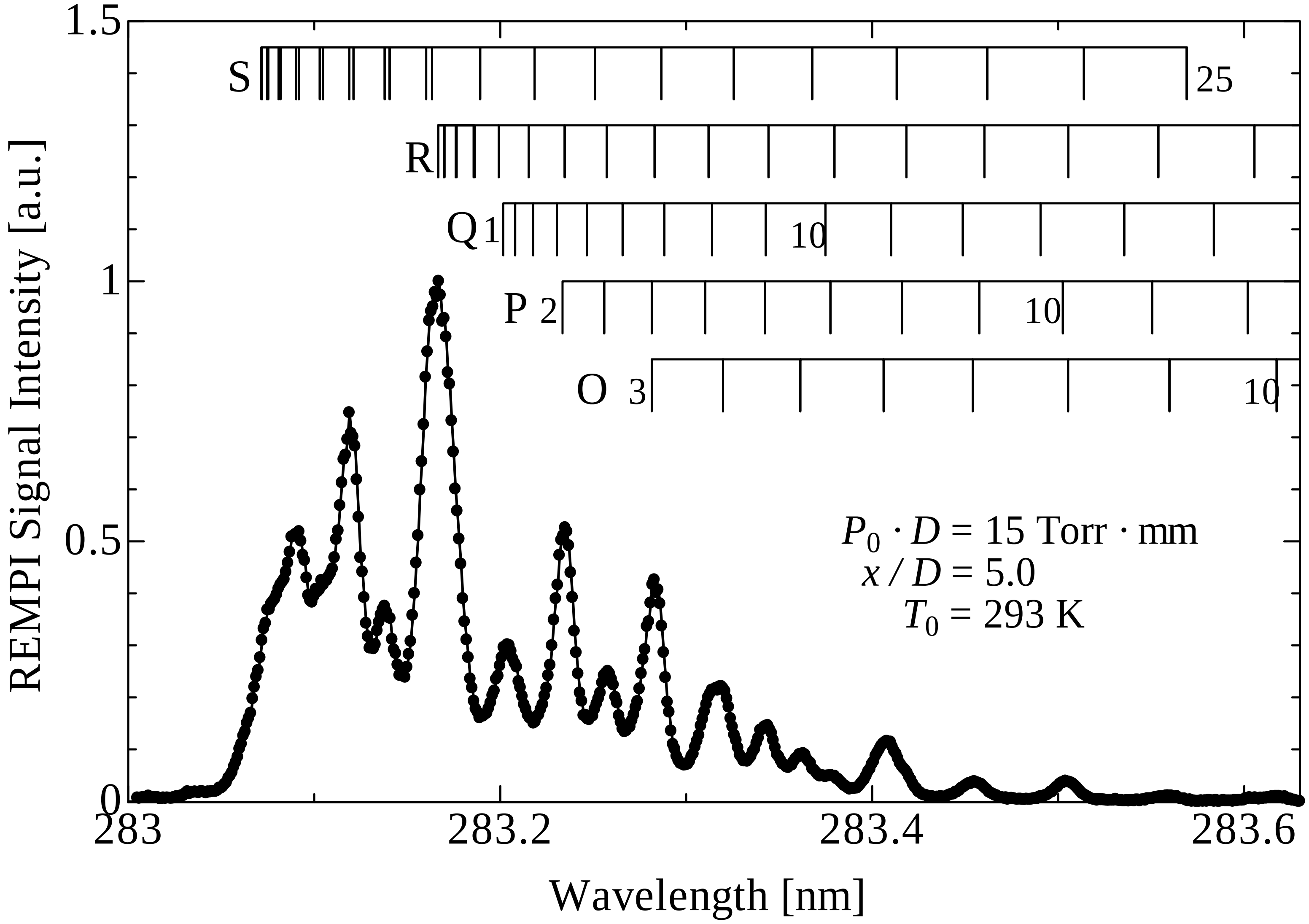
P_0=30, 20, 10, 1 Torr
P_b=1.0x10^{-3}-3.3x10^{-5} Torr
T_0=293 K

P_0D=15, 10, 5, 0.5 Torr-mm

Ion detection

Secondary electron multiplier (P_0=1 Torr)
Tungsten Langmuir probe (P_0≥10 Torr)

REMPI Spectrum



Step of wavelength: 0.001 nm

Boltzmann Plots

Rotational line intensity $I_{J',J''}$ in 2R+2 N_2 -REMPI spectra

$$I_{J',J''} = Ag(J'')S(J',J'')N(J'')/(2J''+1)$$

J : rotational quantum number

(J' : resonant state J'' : ground state)

A : proportional constant independent of the rotational quantum

$N(J'')$: population number

$g(J'')$: nuclear spin statistical weight (3 and 6 for odd and even J'')

$S(J',J'')$: two-photon Hönl-London factor

$N(J'')$ is proportional to $(2J''+1)\exp(-E_{rot}/kT_{rot})$, provided that the rotational energy distribution follows the Boltzmann distribution.

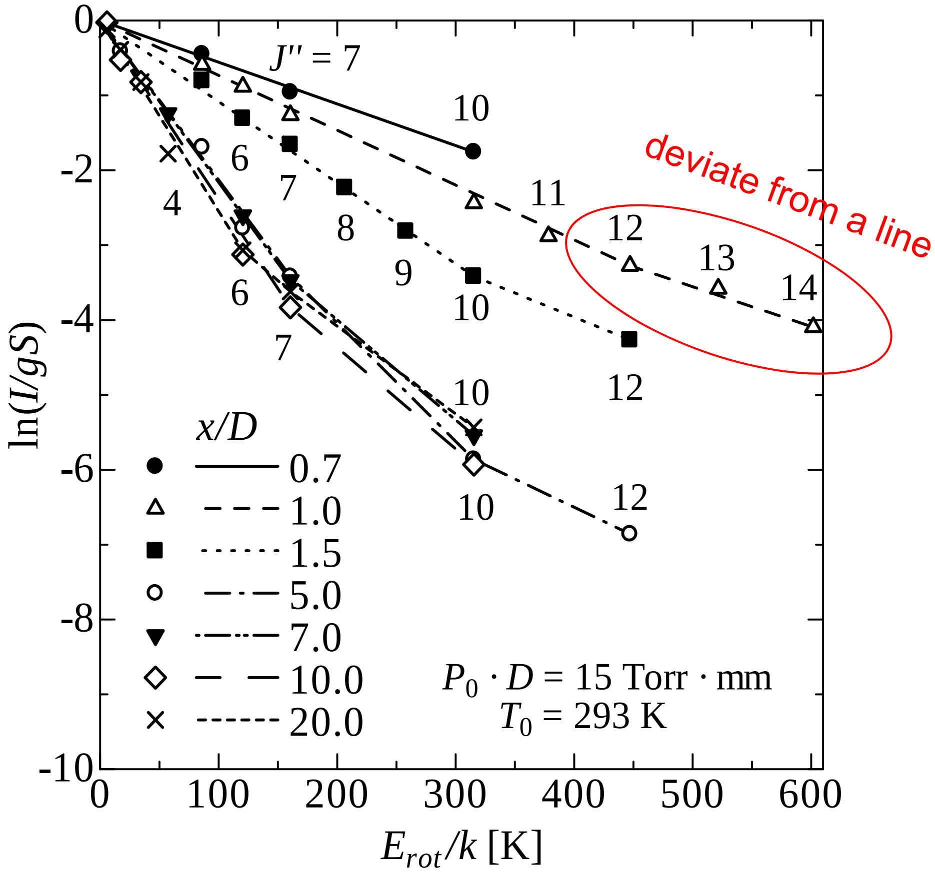
$$I_{J',J''} = Ag(J'')S(J',J'')\exp(-E_{rot}/kT_{rot})$$

Rotational temperature : slope of Boltzmann plot [$\ln(I_{J',J''}/gS)$versus E_{rot}/k],
provided to be in equilibrium.

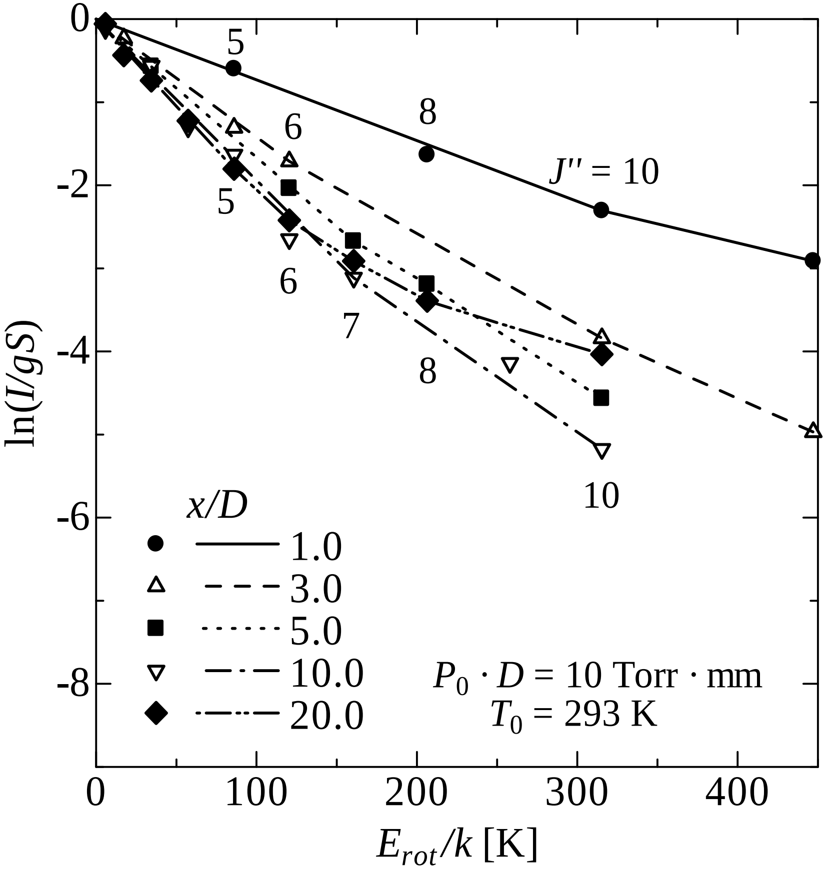
Nonlinearity in the Boltzmann plot :

Rotational energy distribution deviates from the Boltzmann distribution
(Non-Boltzmann distribution) → Rotational temperature cannot be defined.

Boltzmann Plots



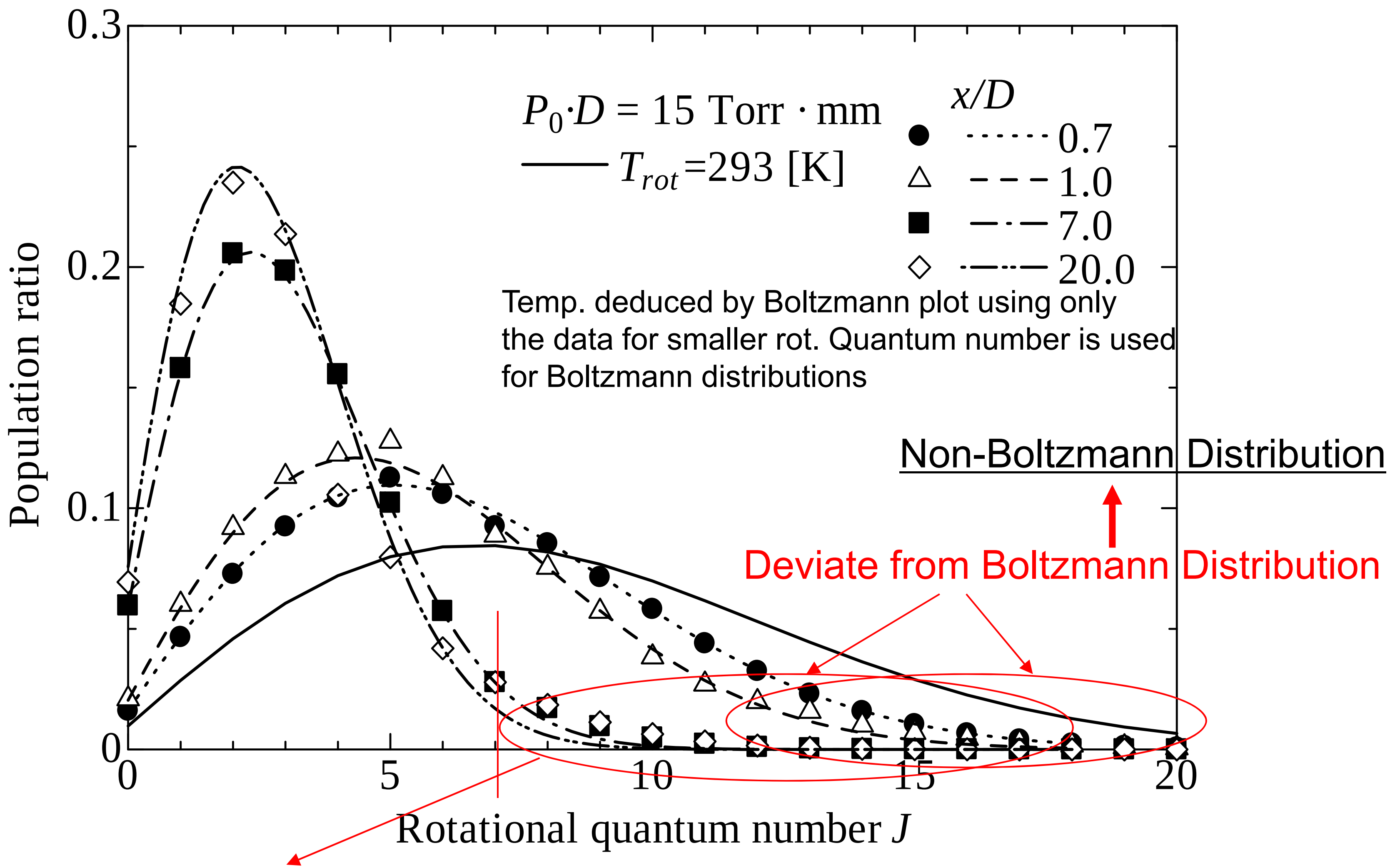
P_0D=15 Torr-mm



P_0D=10 Torr-mm

Determination of the rotational temperature by using only the linear portion of the plots lying at smaller rotational quantum numbers

Rotational Energy Distribution ($P_0 \cdot D$ = 15 Torr·mm)



Temp. deduced by Boltzmann plot using only the data for smaller rot. Quantum number is used for Boltzmann distributions

Non-Boltzmann Distribution

Deviate from Boltzmann Distribution

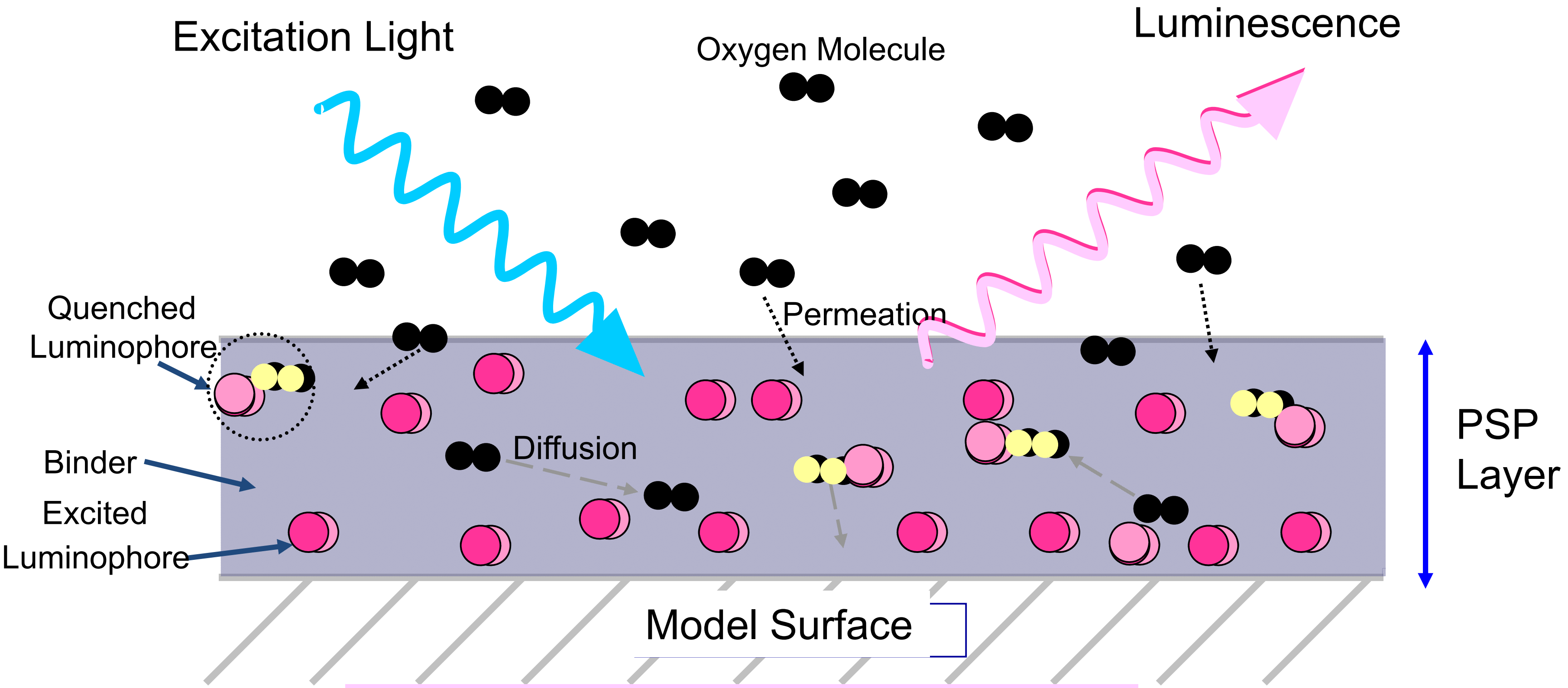
distributions of x/D=7.0 and 20.0 for *J”>7* shows the same tendency

→ partial freezing of the rot. population

H.Mori, T.Niimi et al.,Phys. Fluids 17, 117103 (2005)

Development of PSP for Low Density Gas

Principle of PSP (Pressure Sensitive Paint)



Brighter region: Low pressure region
Darker region : High pressure region

Application of PSP in low-pressure regime is very few, because luminescence intensity does not change significantly in low- pressure range.

→ overcome the limitation of sensitivity!

PSP in Low Pressure Regime

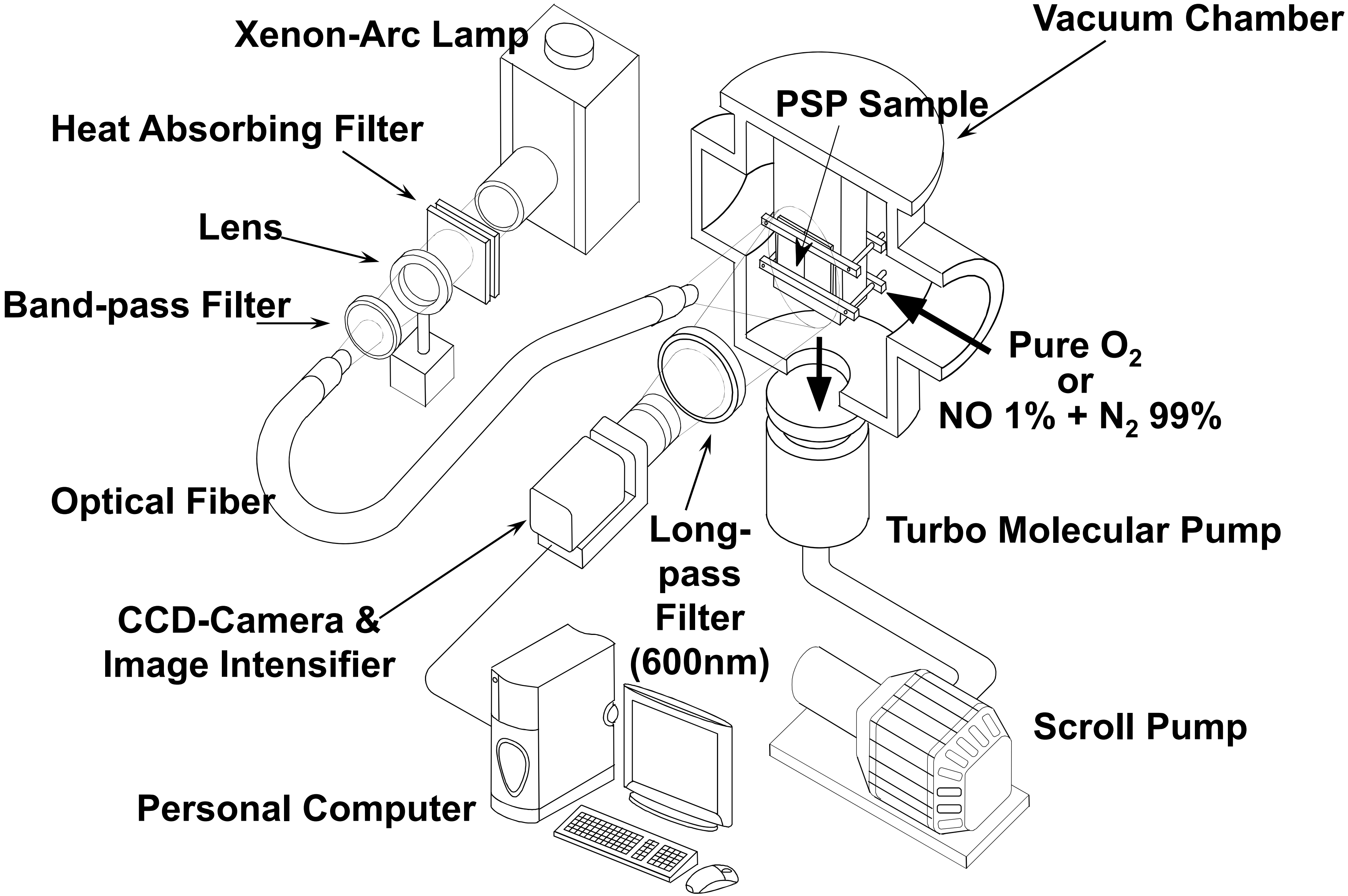
- Sensitivity of PSP is restricted by gas permeability inside the binder layer

  PSPs have been regarded to be inappropriate for use in low pressure regime, because change of luminescence intensity is small.

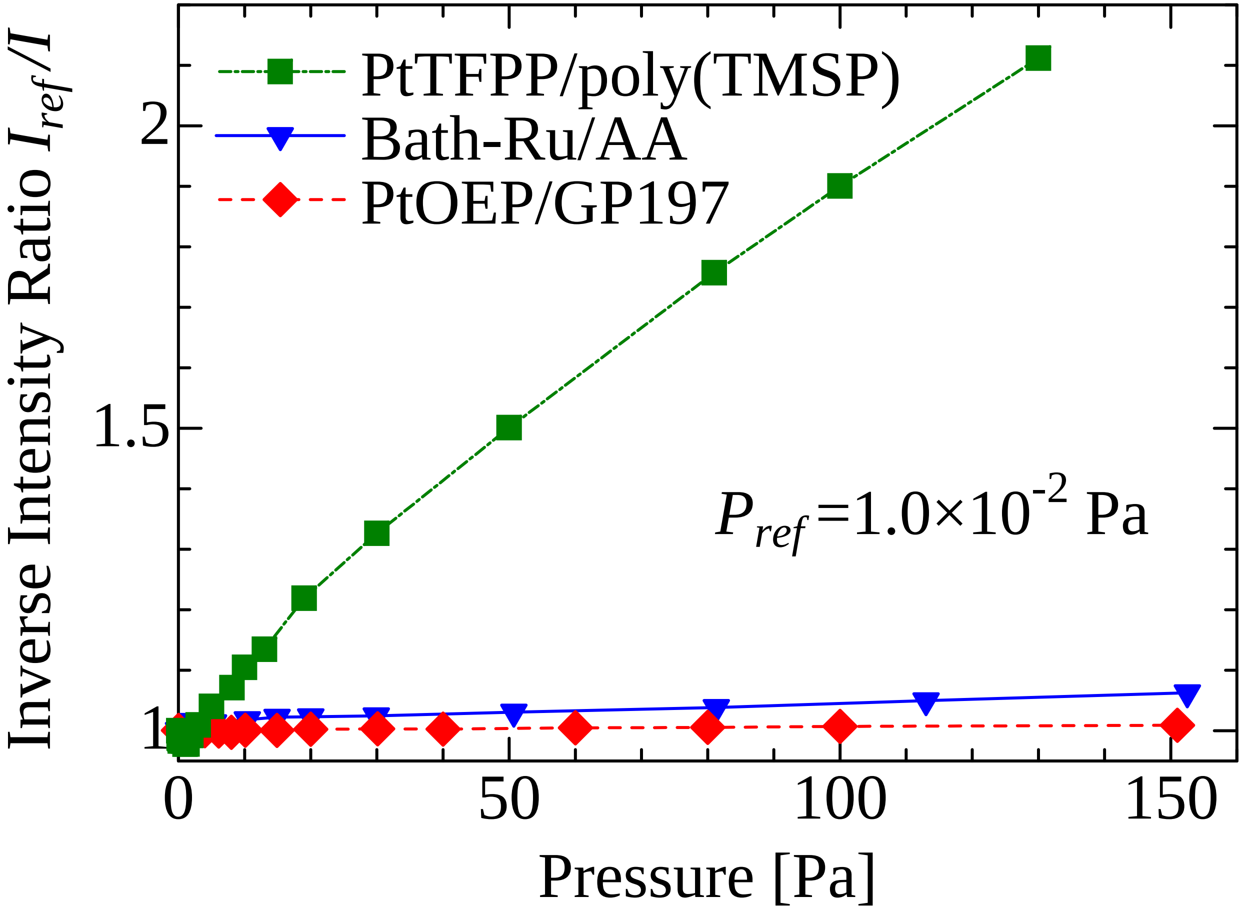
  We have to overcome the limitation of sensitivity!

- 1st step: suitable binder?
  - Porous surface of anodized aluminum (AA):
    luminescent molecules are bound directly on the surface
    ➔ exposed to the atmosphere : Bath-Ru/AA
  - poly(TMSP):
    glassy polymer with extremely high oxygen permeability :PtTFPP/poly(TMSP)
  - (PtOEP/GP197: tested for comparison)

Experimental Apparatus



PSP in Low Pressure Regime



PSP in Low Pressure Regime

- PtTFPP/poly(TMSP): high sensitivity

  ⇐ high oxygen permeability of poly(TMSP)

- Bath-Ru/AA:
  - lower sensitivity than PtTFPP/poly(TMSP)
  - time delay for abrupt pressure change

  ⇐ Adsorption and desorption of oxygen molecules inside pores

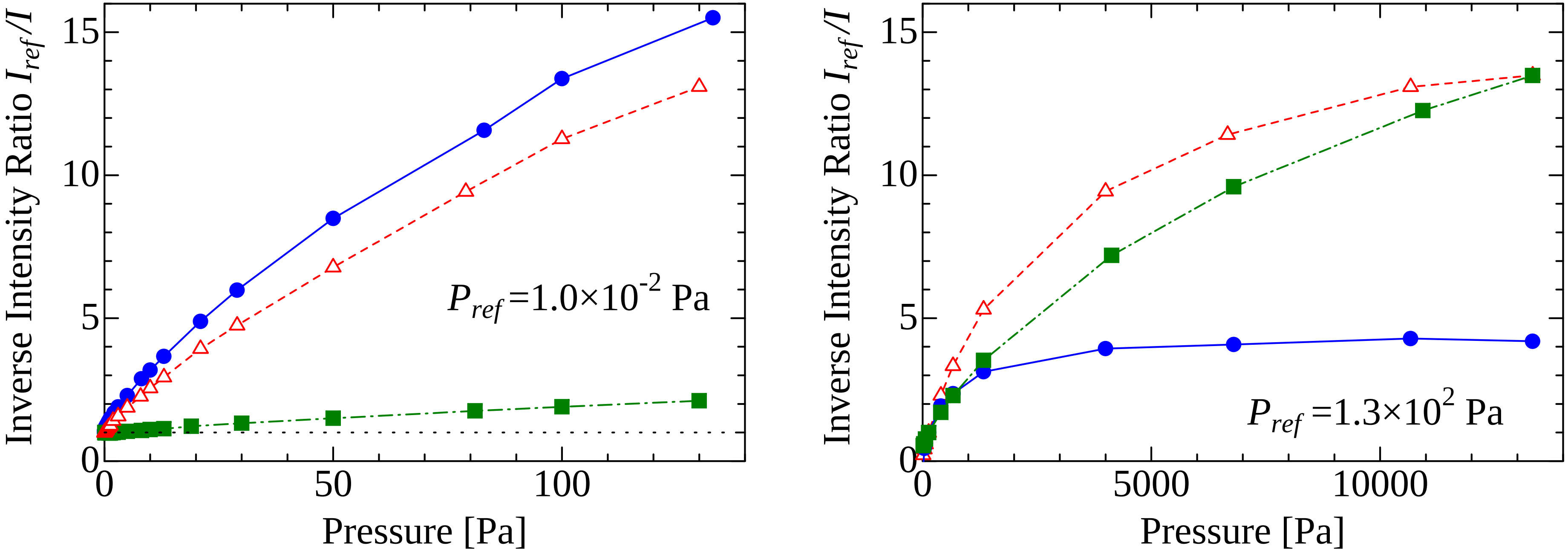
- PtOEP/GP197: no sensitivity

Oxygen Pressure Sensitivity of PSPs using poly(TMSP) as a Binder

- 2nd step:
  Luminophore with high sensitivity to combine with the binder poly(TMSP)?
  - PtTFPP (has been used)
  - PdOEP
  - PdTFPP

Oxygen Pressure Sensitivity of PSPs using poly(TMSP) as a Binder

✦ Luminophore: PdTFPP --△-- PdOEP —●— PtTFPP -·■·-



(a) 1.0 × 10^{-2} – 1.3 × 10^{2} [Pa] below 1 Torr (133.3 Pa)

(b) 1.3 × 10^{2} – 1.3 × 10^{4} [Pa] wide range of pressure (1 – 100 Torr)

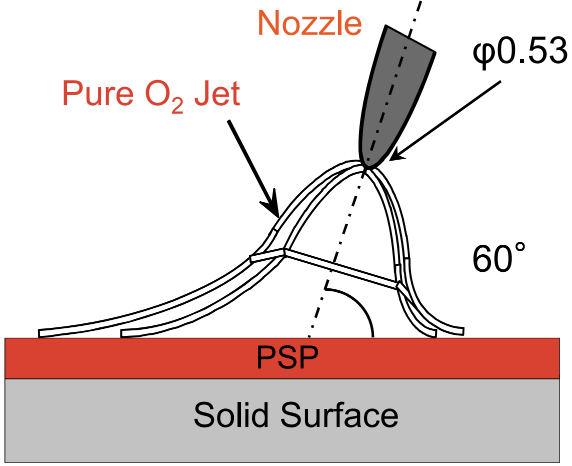
Oxygen Pressure Sensitivity of PSPs using poly(TMSP) as a Binder

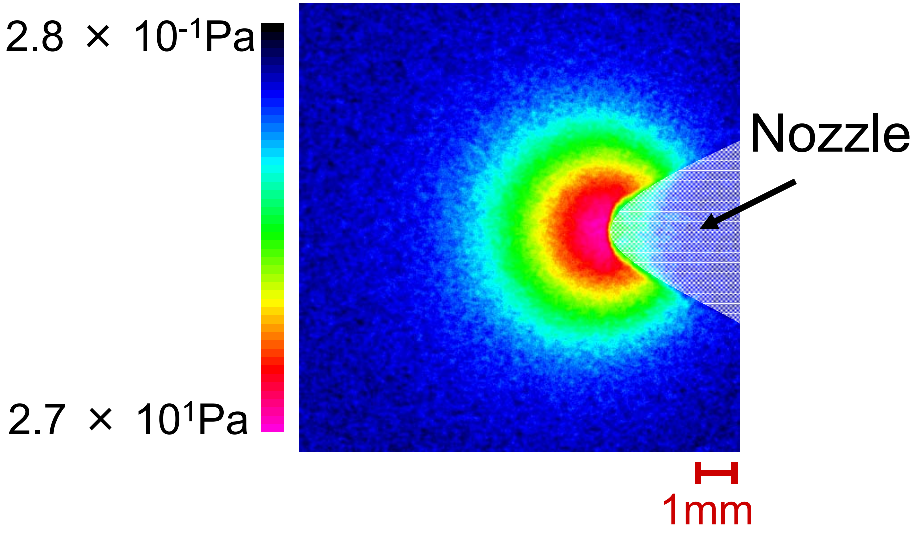
- PdOEP or PdTFPP / poly(TMSP)
  - very powerful measurement tool at low pressure (< 1 Torr)
  - not suitable above 1 Torr (133Pa)
- PtTFPP / poly(TMSP)
  - useful at relatively wide pressure range (up to 100 Torr)

Pressure Distribution on a Solid Surface interacting with Low Density Gas Flow

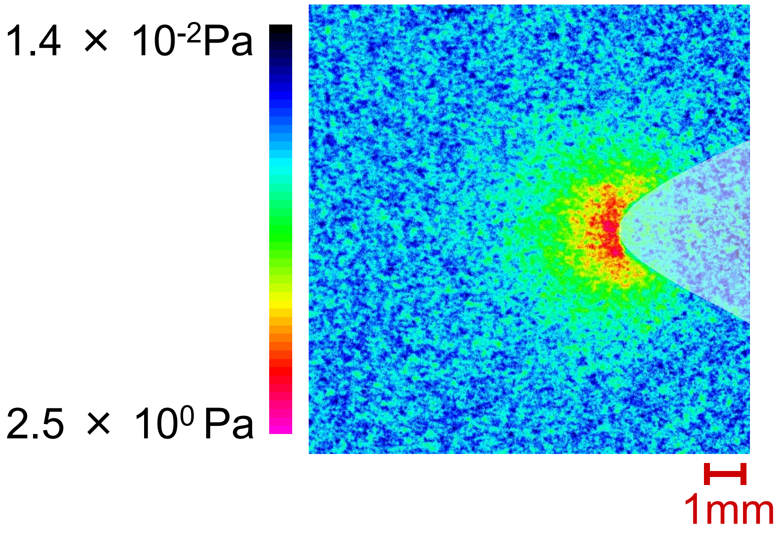
- PSP:PdOEP/poly(TMSP), test gas: oxygen

P_s: Source Pressure
P_b: Background Pressure





(a) $P_s = 1.3 \times 10^3$ Pa (10 Torr)
$P_b = 1.3$ Pa (0.01 Torr)



(b) $P_s = 1.3 \times 10^2$ Pa (1Torr)
$P_b = 7.7 \times 10^{-2}$ Pa

Pressure distribution below 1 Torr is detected !

Development of PSMF for Micro- and Nano-Devices
(PSMF: Pressure Sensitive Molecular Film)

LB Method for Fabrication of PSMF
Application of PSMF to Micro-Flow

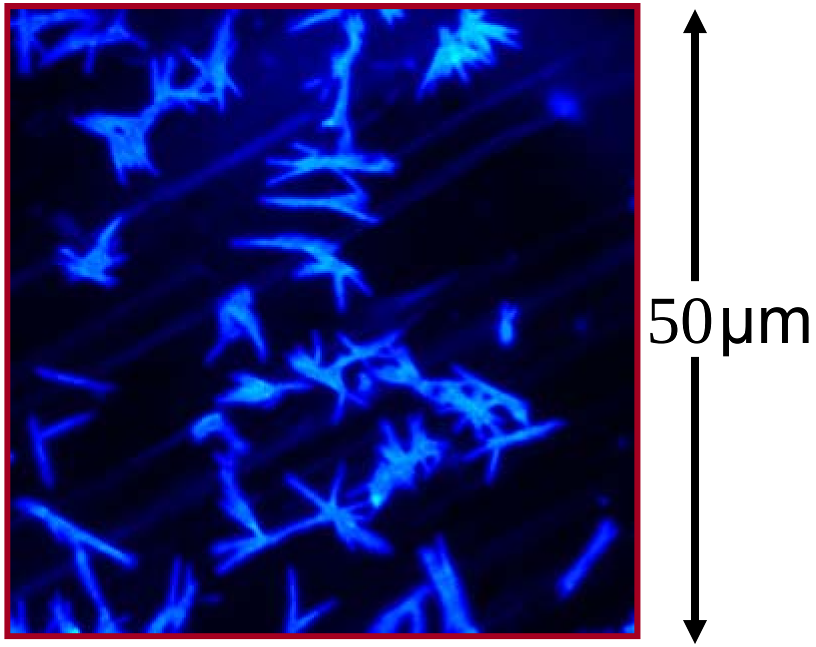
Conventional PSP

Some problems for

High Knudsen Number Flows

(the flow fields around micro- or nano-devices)

- Large thickness (>5μm)
- Large surface roughness (~μm)
- Low spatial resolution due to aggregation of luminescent molecules



Aggregation of luminescent molecules in the layer

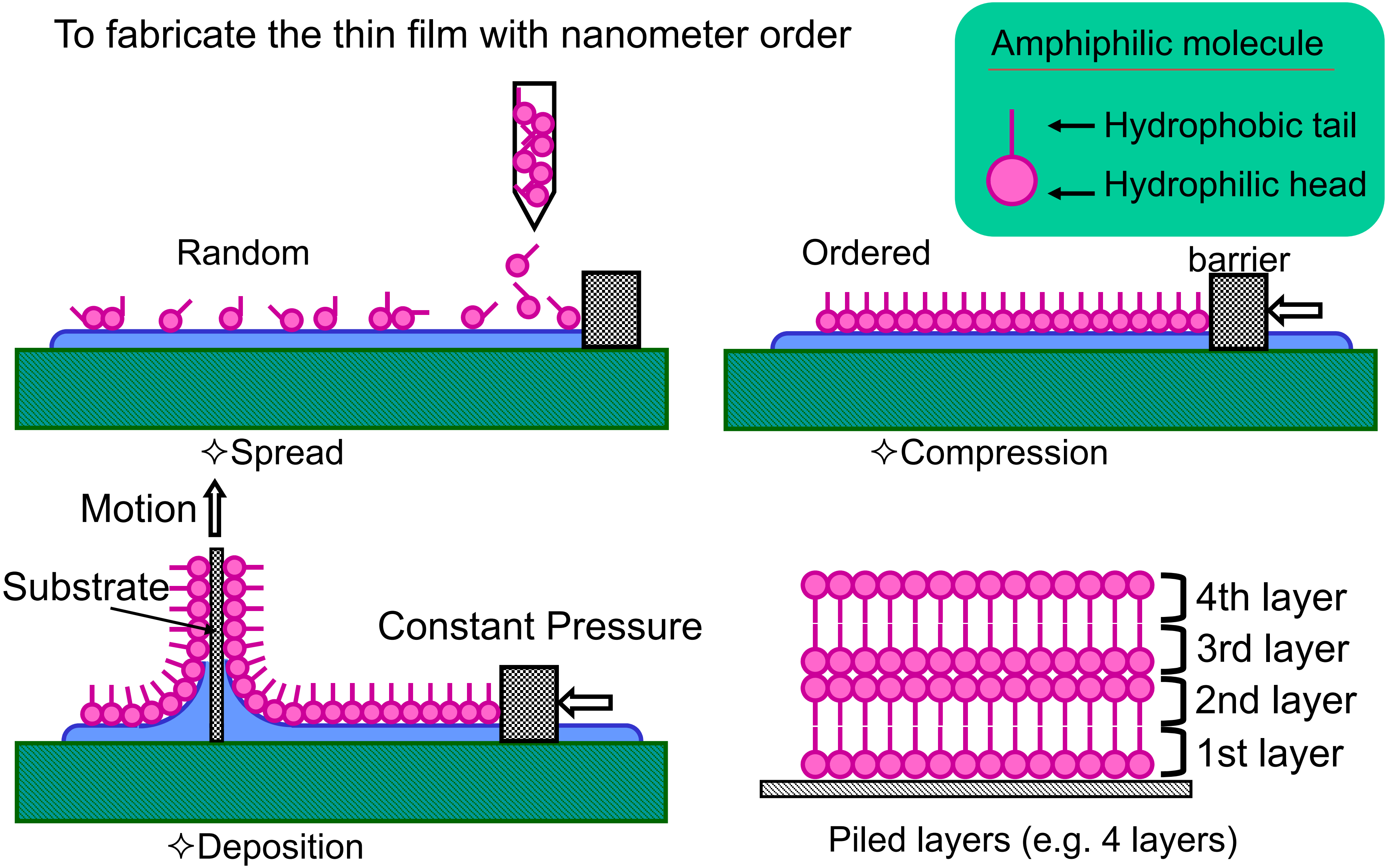
For High Knudsen Number Flows:

PSMF（Pressure Sensitive Molecular Film）

with nanometer order thickness and ordered molecular structure

Langmuir-Blodgett Method

To fabricate the thin film with nanometer order

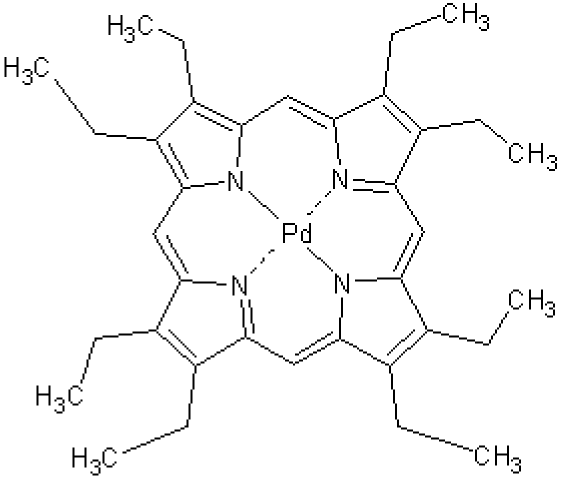


Piled layers (e.g. 4 layers)

Component of PSMF

- PdOEP（Pd(II) Octaethylporphine）

  -conventional PSP composed of PdOEP
  high sensitivity in low pressure regime
  -hydrophobic molecule
  difficult to fabricate a stable LB film

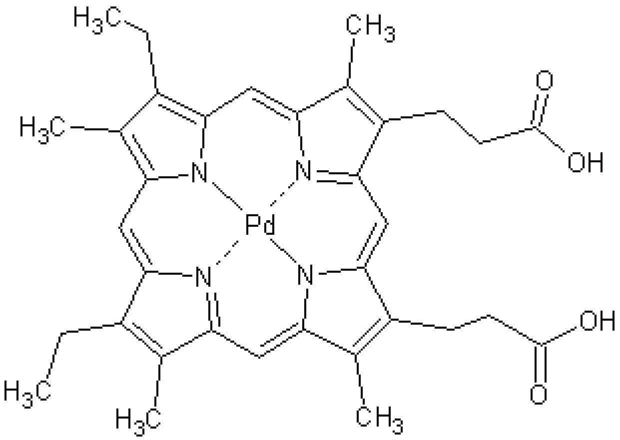


PdOEP

- PdMP（Pd(II) Mesoporphyrin IX）

  -amphiphilic molecule
  -stable LB film can be obtained

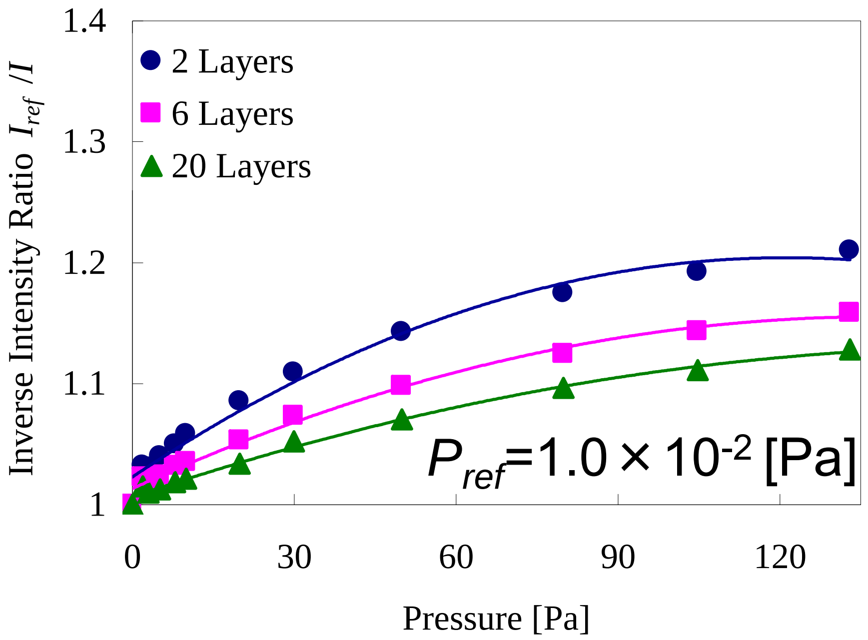
prepare three types of samples 2,6 and 20 layers of PSMF to test their pressure sensitivity



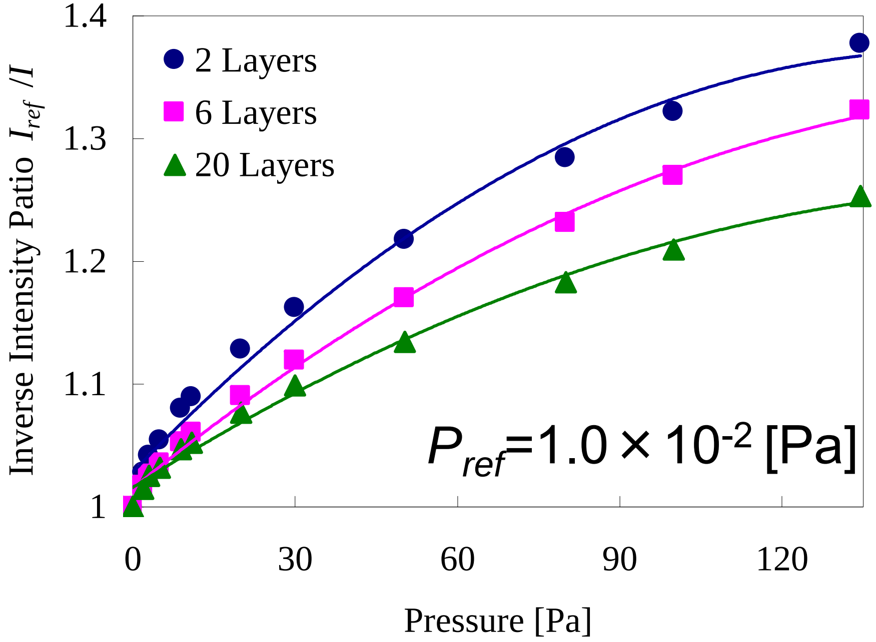
PdMP

Pressure Sensitivity

PdOEP



PdMP

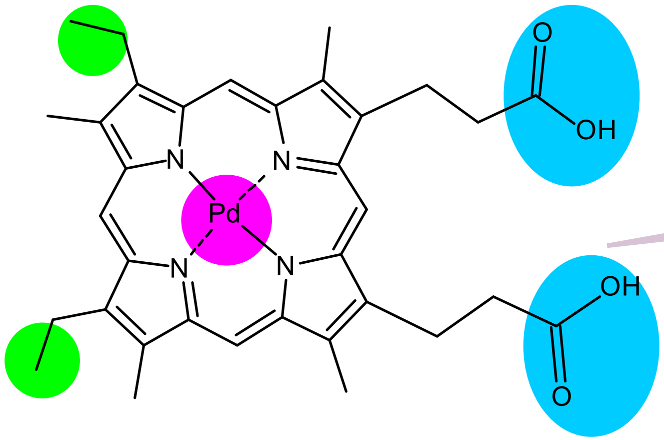


PSMF composed of PdMP has higher sensitivity than that of PdOEP
The sensitivity of 2-layer PSMF is higher than the others

PSMF has sufficient sensitivity in the low pressure regime with high Knudsen number

Y. Matsuda et al., *Experiments in Fluids* Vol.42, No.4, pp.543-550 (2007)

PSMF with Higher Pressure Sensitivity in Atmospheric Condition



Applicable Pressure Range
<130Pa (pure O_2)

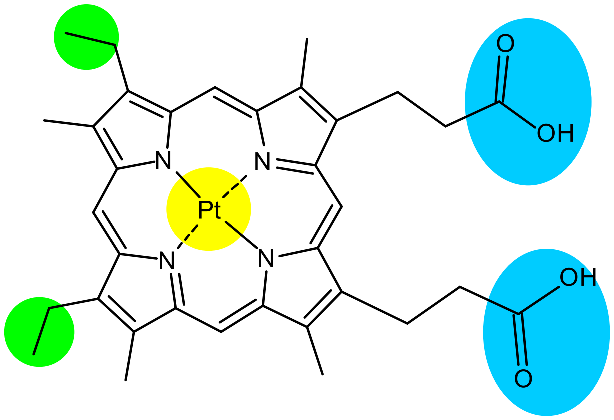
Pd(II)Mesoporphyrin IX
(PdMP)

MEMS Device
used in Atmospheric Condition

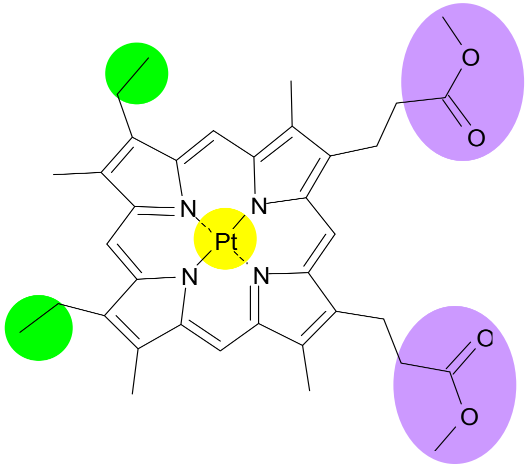
Develop New PSMF
with Higher Pressure Sensitivity
in Atmospheric Condition

Candidates of luminescent molecule for PSMF
PtMP, PtMP-DME, PtPP, CuMP-DME

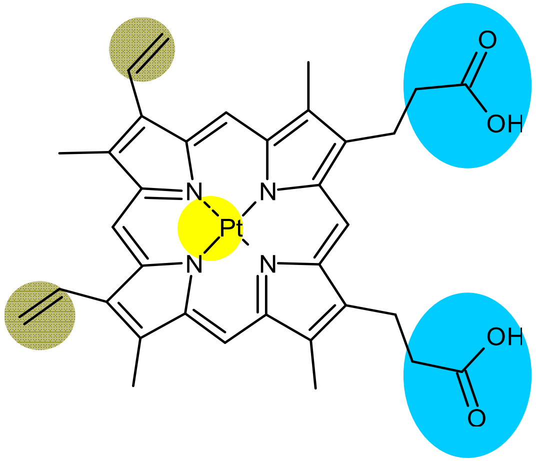
Luminescent Molecules



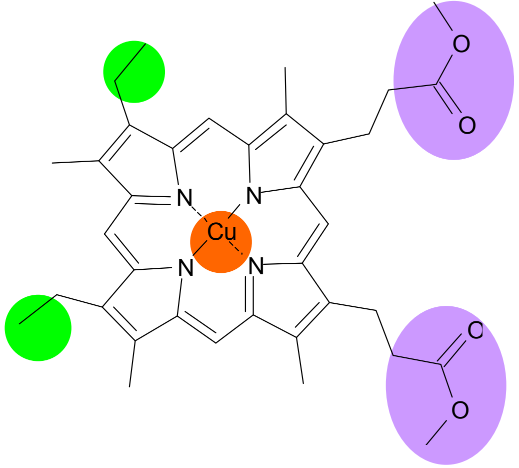
Pt(II)Mesoporphyrin IX (PtMP)



Pt(II)Mesoporphyrin IX-DME (PtMP-DME)



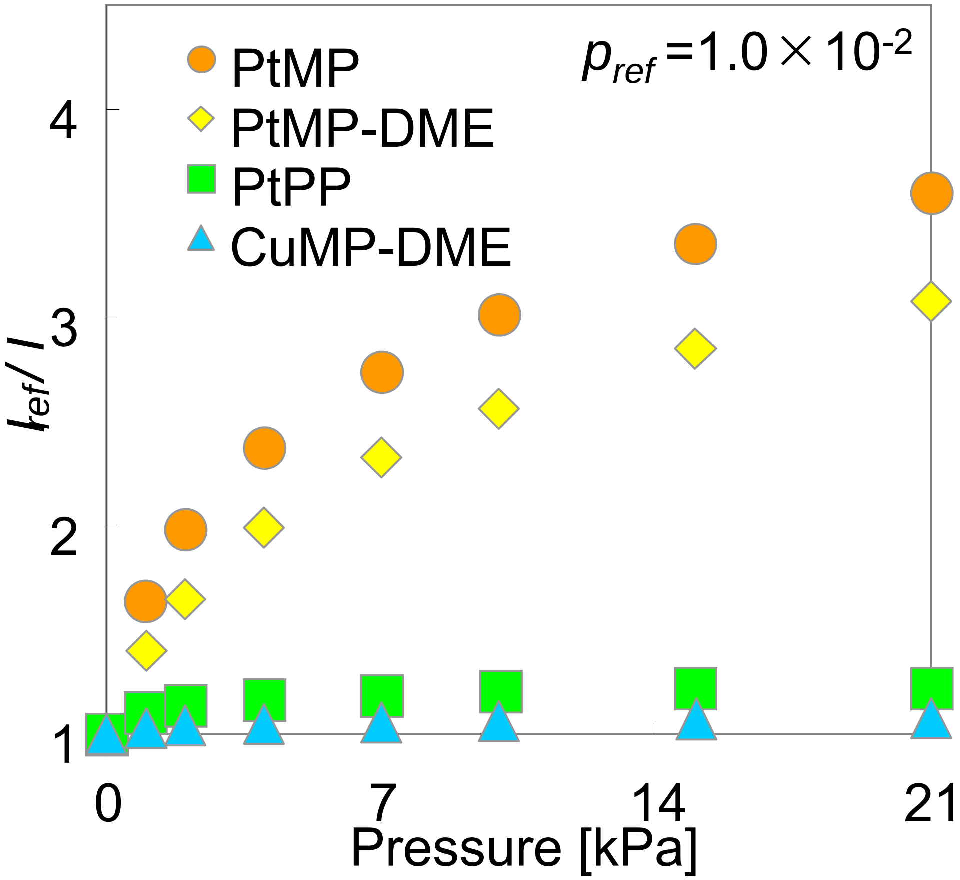
Pt(II)Protoporphyrin IX (PtPP)



Cu(II)Mesoporphyrin IX-DME (CuMP-DME)

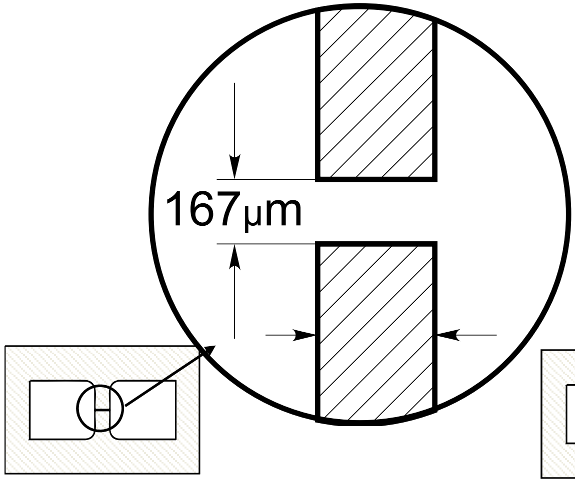
→ prepared 6-layers of PSMF for each luminescent molecule to test the pressure sensitivity in the range of pressure up to 21 kPa, partial pressure of oxygen in air

Stern-Volmer plot

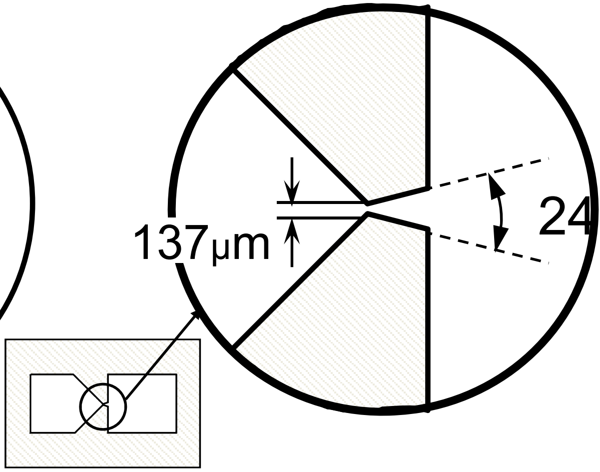


PtMP has the highest pressure sensitivity below 21kPa

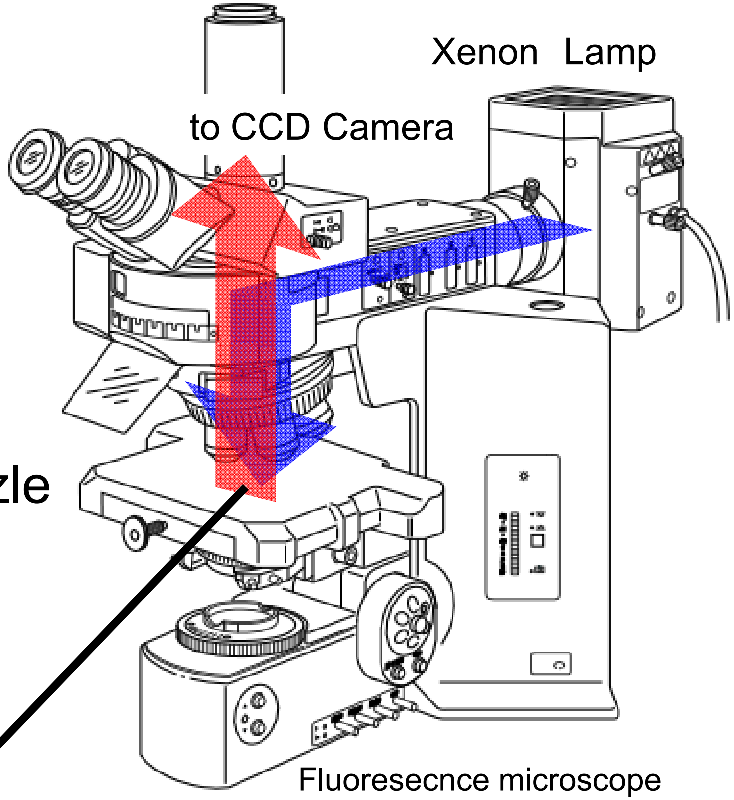
Applications of PSMF to Micro-Scale Channel and Nozzle



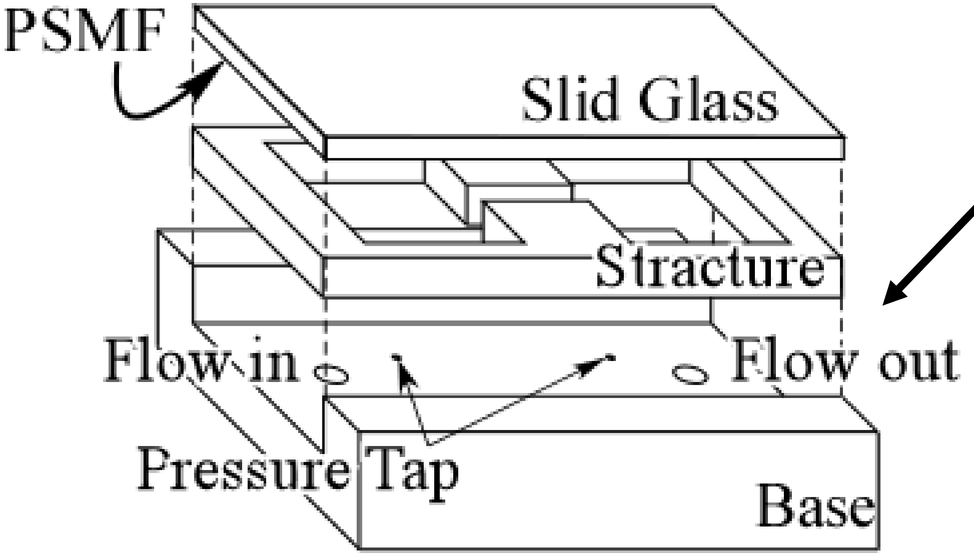
Micro-Channel



Micro-Conical Nozzle



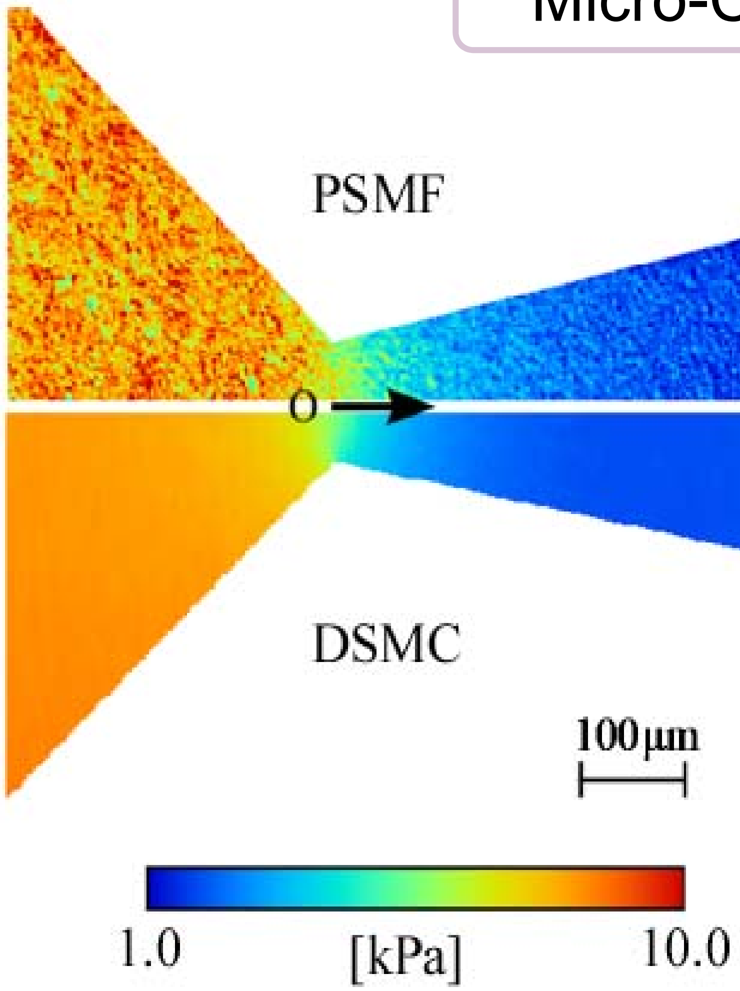
Fluoresecnce microscope



Excitation Filter	400±20nm
Dichroic Mirror	500nm
Absorption Filter	600nm

Pressure distribution measured by PSMF

Micro-Conical Nozzle



- PSMF • • • PSMF-PtMP 6-layer
- Gas • • • O_2 21.0%, N_2 balance
- Source pressure • • • 10.0kPa
- Back pressure • • • 1.0kPa

Y. Matsuda et al, Microfluidics and Nanofluidics,10, No.1, pp.165-171, 2011

Applications of PSP [PtTFPP/poly(TMSP)] in atmospheric condition

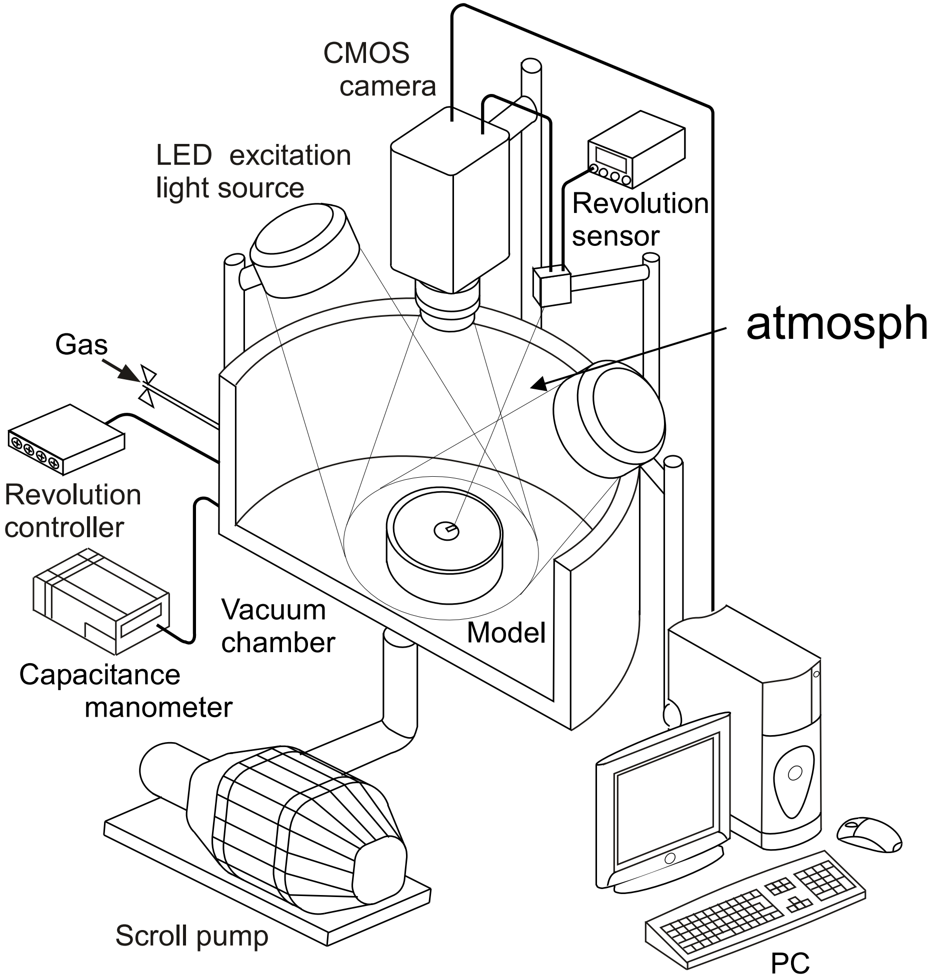
Rotating Disks

Surface Pressure Distribution on Rotating Disks

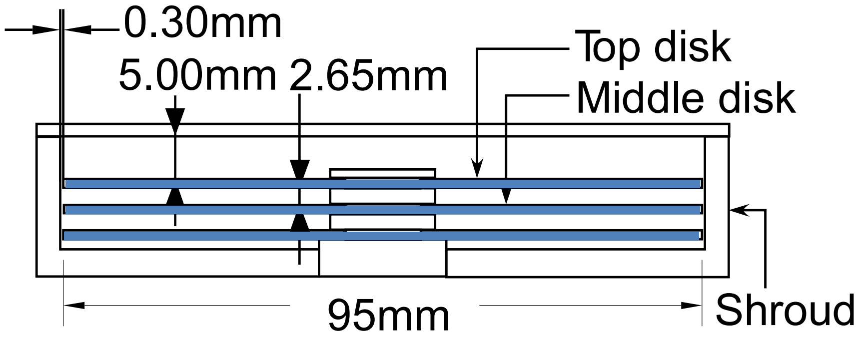
Mixing Chamber

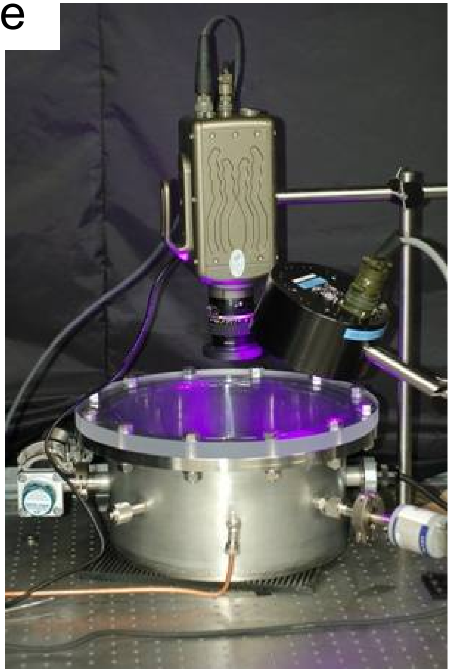
Density Fluctuation at Interface of Interacting Parallel Two Jets

Experimental Setup

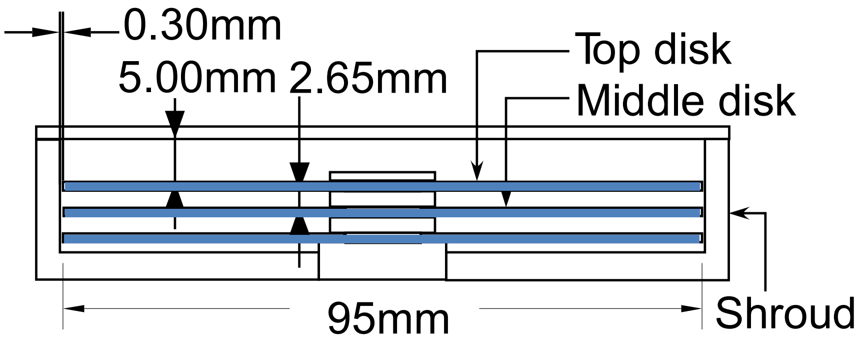


Three Disks
PSP is painted on Top and Middle Disks



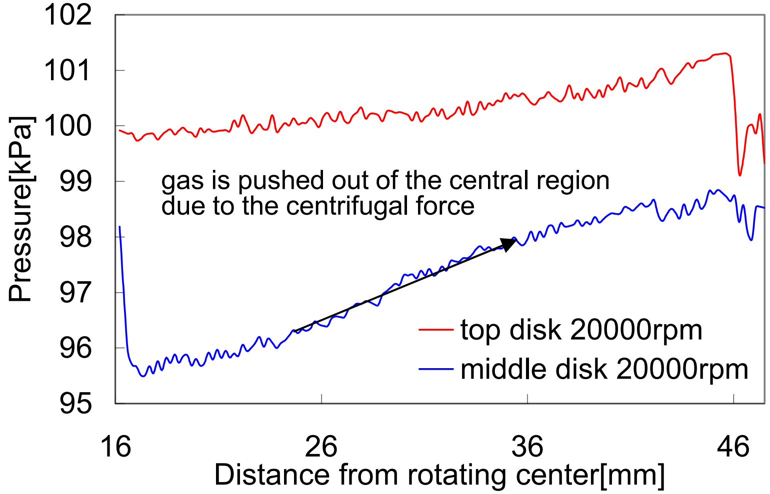


Surface Pressure Distribution on Rotating Disks

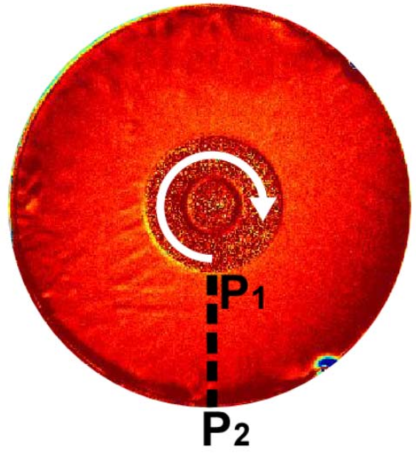


Experimantal conditions

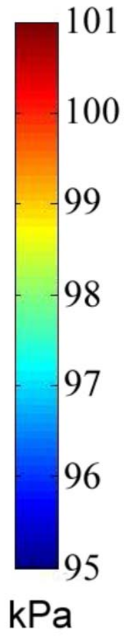
Disk Diameter : 95mm
PSP: PtTFPP/poly(TMSP), TiO_2 2.0g/l
Carrier Gas : $N_2$79%, $O_2$21%
Rotating Speed (I) : 20000rpm
Rotating Speed of Reference Image (I_{ref}) :300rpm
Integration Time:20ms
Ambient Pressure :100kPa

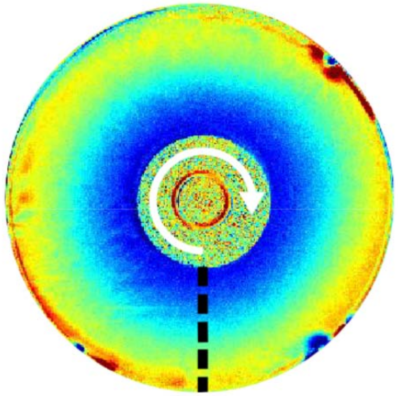


gas is pushed out of the central region due to the centrifugal force



Top Disk $\Delta P=P_2-P_1=1.5$kPa





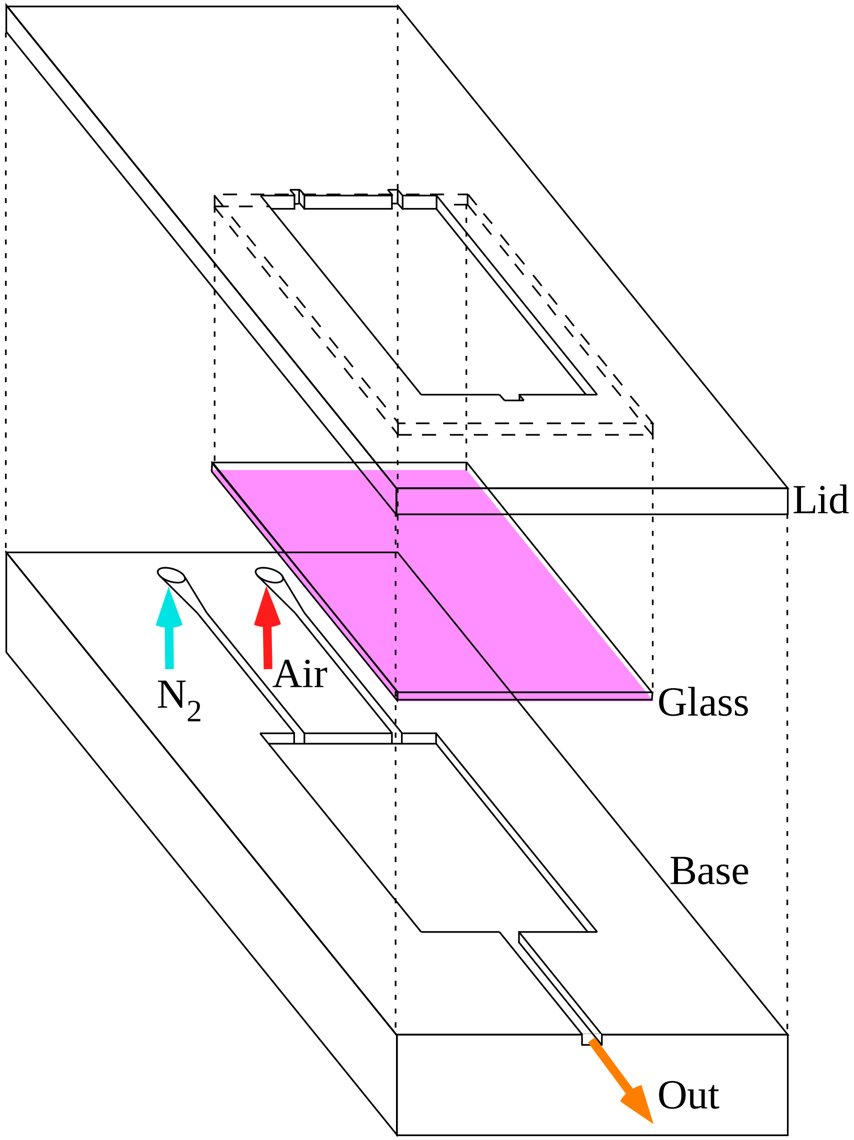
Middle Disk $\Delta P=3.0$kPa

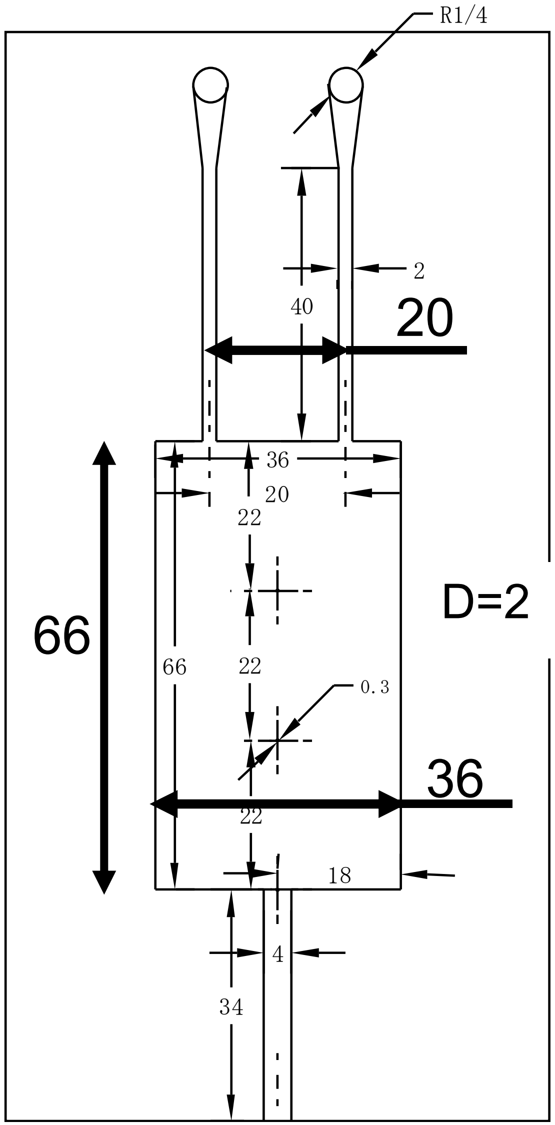
Applications of PSP [PtTFPP/poly(TMSP)] in atmospheric condition

Mixing Chamber

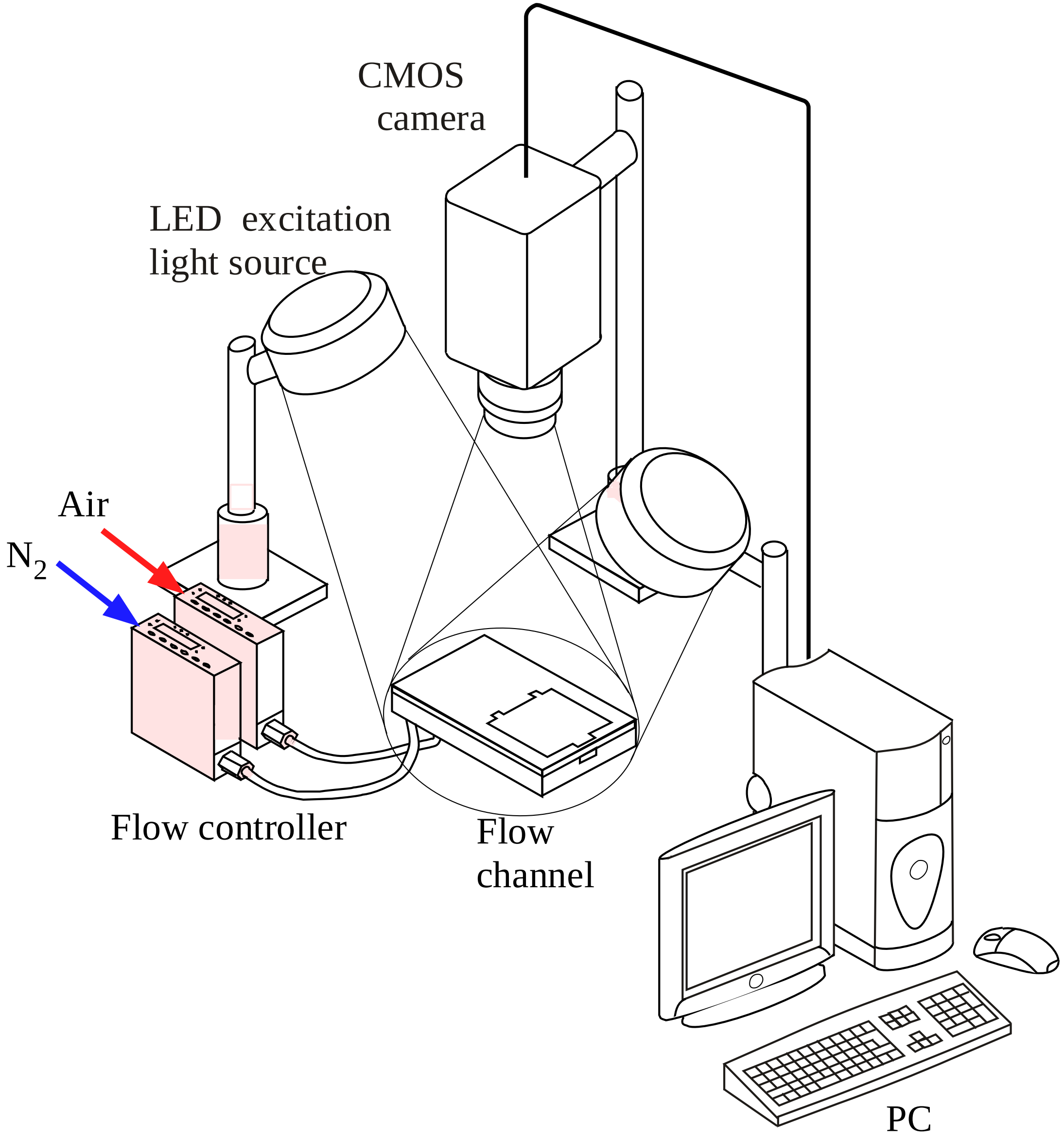
Density Fluctuation at Interface of Interacting Parallel Two Jets

Mixing Chamber





Experimental Setup



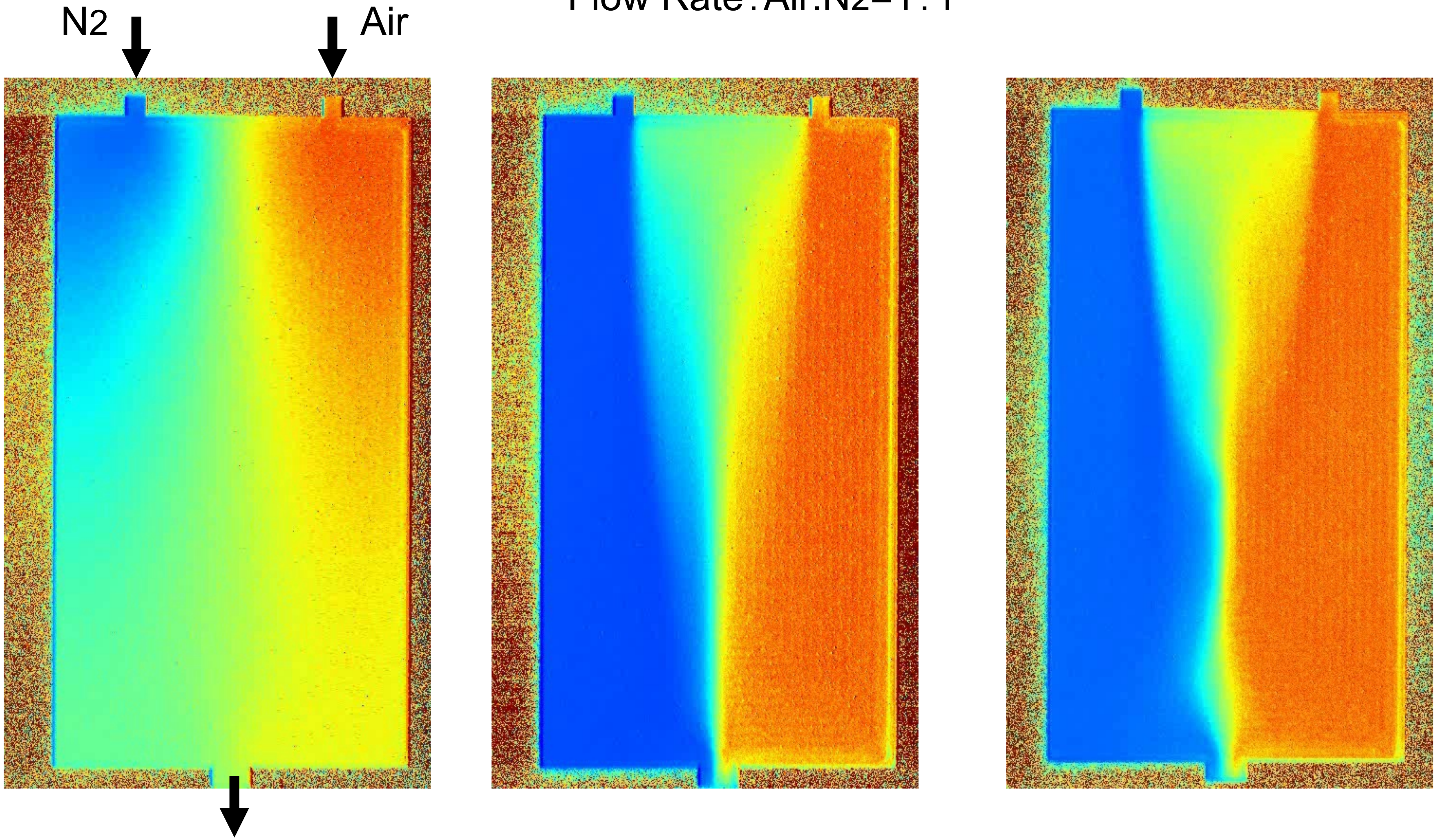
PSP
PtTFPP/poly(TMSP)
- Relatively high sensitivity around atmospheric pressure
- High Oxygen Permeability,
- Quick Time Response

Flow controller
Digital Mass Flow Cotroller
MQV0002(Yamatake Co. Ltd.)

Flow Rate：20ml/min~2000ml/min
Accuracy：±10ml/min
(Q=20~1000ml/min)
±20ml/min
(Q=1000~2000ml/min)
Response Time：0.3s

Experimantal Results

Flow Rate：Air:N2=1：1



Re=10(Q=20ml/min)　　Re=550(Q=1000ml/min)　　Re=830(Q=1500ml/min)

Summary

1. High Knudsen Number Flows
2. Development of Optical Diagnostics Methods for High Knudsen Number Flows
    - Laser Induced Fluorescence (LIF) :
    - Resonantly Enhanced Multi-Photon Ionization (REMPI)
        - Rotational Nonequilibrium in Low Density N2 Jets
3. Application of Pressure Sensitive Paint (PSP) to High Knudsen Number Flows
    - Applications of PSP to Low Density Gas Flows,
    - Development of PSMF for Micro- and Nano-Devices (PSMF: Pressure Sensitive Molecular Film)
        - LB Method for Fabrication of PSMF
        - Application of PSMF to Micro-Flows
4. Applications of PSP in Atmospheric Condition
    - Rotating Disks
    - Mixing Chamber