

# PAHs Emission on-line Monitoring by Proto-type Jet-REMPI-TOFMS

Shun-ichi Hayashi<sup>1</sup>, Tetsuya Suzuki<sup>2</sup>, Michihiro Aimoto<sup>1</sup>, Shun-ichi Ishiuchi<sup>3</sup> and Masaaki Fujii<sup>3</sup>

<sup>1</sup>Nippon Steel Corp., <sup>2</sup>Nippon Steel Techno Research Corp., <sup>3</sup>Tokyo Institute of Technology JAPAN

## INTRODUCTION

Due to the adverse health effects of the polycyclic aromatic hydrocarbons (PAHs) emitted by diesel vehicles, the emission regulation are being strengthened. So far, GC/MS was utilized as the standard technique to evaluate the composition of the sample.

However, short time fluctuation of the combustion, which might lead to the dramatic change of the chemical concentration of the specific compound, cannot be observed. As a part of the motivation, we have been developed the proto-type apparatus for the real time monitoring of PAHs based on the Jet-REMPI (Supersonic Jet- Resonance Enhanced Multi-Photon Ionization)-TOFMS technique. Because combustion and pyrolysis products consist of highly complex mixtures containing several hundreds of different species, sophisticated analysis should be required not only to estimate their chemical composition but also to distinguish the isomers which have the much different toxicities.

In addition, PAHs have comparatively higher boiling points, so we designed the newly continuous sample gas introduction system instead of the conventional pulsed valve inlet. And also we improved the ion detection efficiency of the TOF-MS to evaluate PAHs with the concentration of several tens ppb with molecular selectivity.

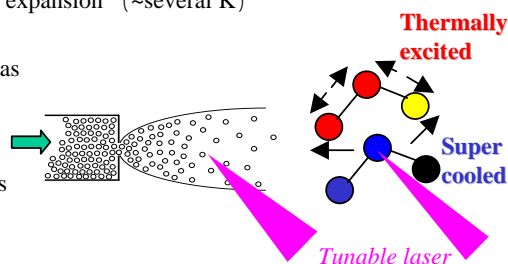
### Principle of Jet-REMPI

Supersonic Jet-Resonance Enhanced Multi-Photon Ionization

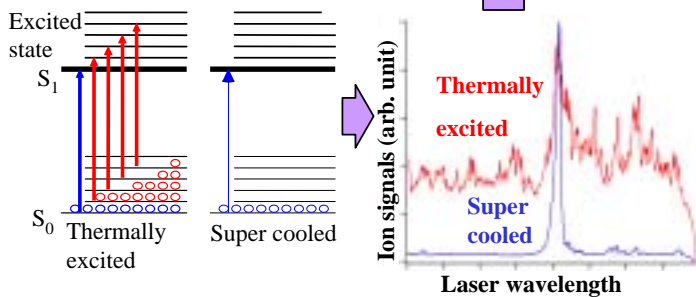
#### Supersonic Jet

in order to quench the thermal motion of the molecule using adiabatic expansion (~several K)

Sample gas involved specific molecules



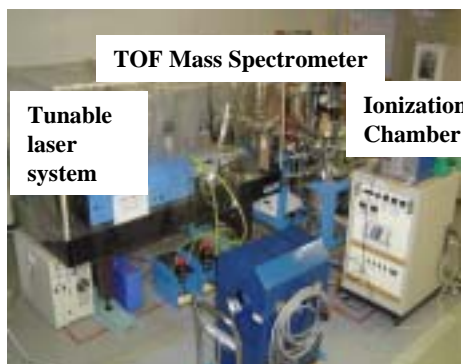
It is very important to make the molecules in the jet cool for molecular selectivity and higher sensitivity.



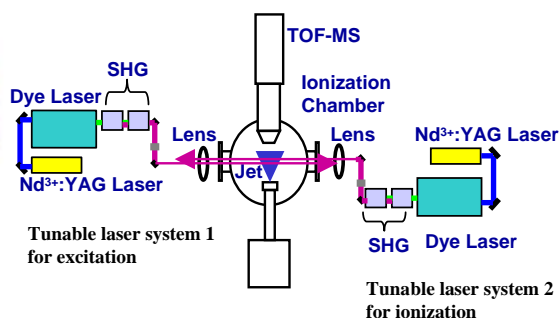
Jet-REMPI technique is expected as a higher-isomer-selectivity, High sensitivity analytical method for the online measurement of the trace amounts of organic compounds in a complex gas mixture. The REMPI technique is based on a laser-induced ionization method using more than two photons. In the case of two Photon process, a first ultraviolet(UV) photon is used for excitation as the electronic state (typically the  $S_1$  state) and the subsequent absorption of a second UV photon raises the internal energy above the of the molecules, thus forming a molecular ion.

This process is significantly enhanced only when the first step is in resonance with an electronically excited state, most preferably the lowest electronic state ( $S_1$ ). The spectral "fingerprint" of this electronic state can be obtained by changing the wavelength of the fine tunable laser and is, in general, molecule specific.

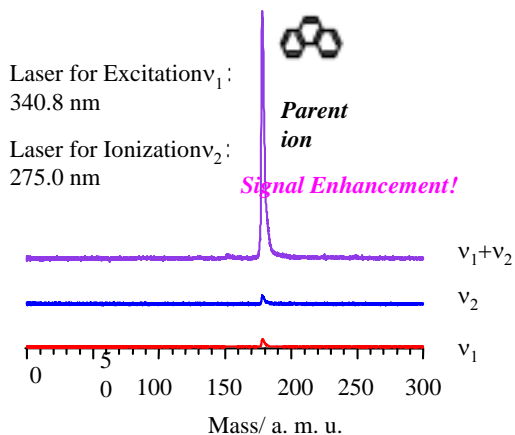
#### Photograph of our Jet-REMPI



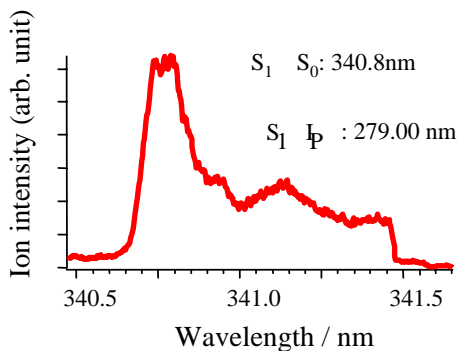
#### Schematic diagram of our Jet-REMPI



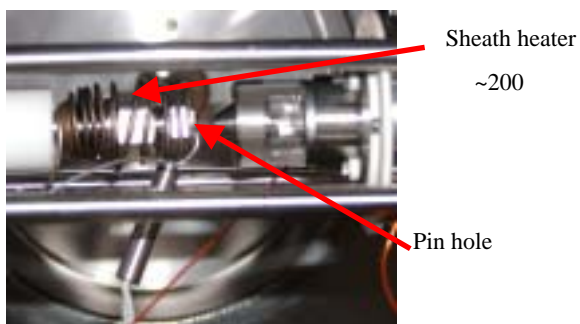
## REMPI Mass Spectra of Phenanthrene



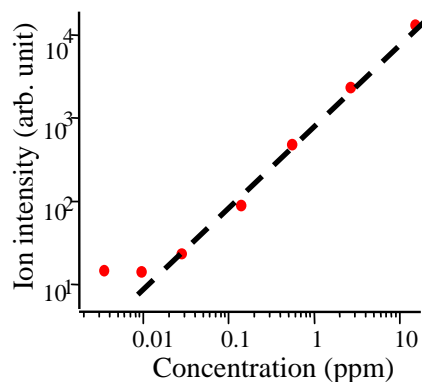
## REMPI spectrum of Phenanthrene



## Sample introduction through the pin hole with heating

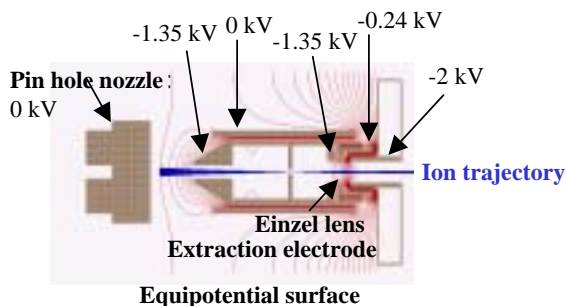


## Calibration curve of phenanthrene taken by REMPI



## Table for Detection limits

	Detection limit (ppb)
Phenanthrene	10
Anthracene	250
Pyrene	50



## CONCLUSION & FUTURE PLAN

We have been developing the real time monitoring apparatus with molecular selectivity and higher sensitivity for detection of PAHs and applying it for the quantification of PAHs. As the results, the detection limits of phenanthrene, anthracene and pyrene were evaluated about 10ppb, 250 ppb, and 50 ppb, respectively. Further research for getting higher sensitivity, e.g. introduction of the pulse counting system, are required and it is expected the direct combination with chassis dynamometer and the estimation of the relations of the emission of PAHs with the particulate matters, CO, Hydrocarbon and NOx at the next stage.

# PAHs Emission on-line Monitoring by Proto-type Jet-REMPI-

## TOFMS

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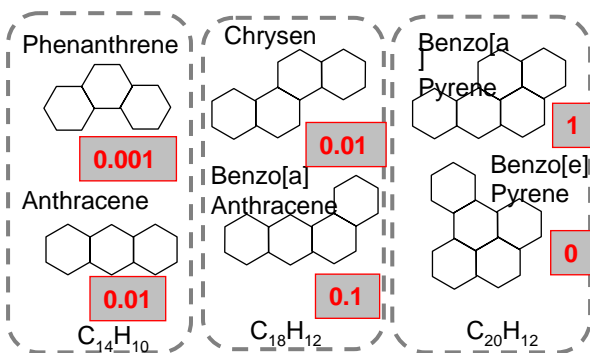
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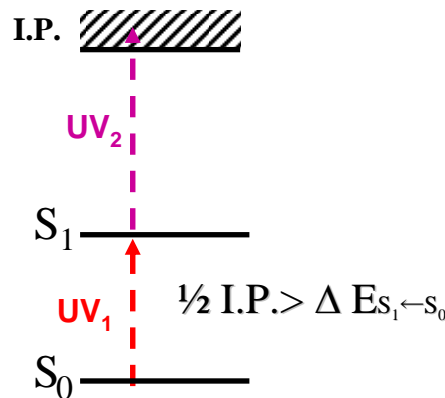
### Toxicities of PAHs



Nisbet, I. C., and Lagoy, P. K.,

Regulatory Toxicology and Pharmacology 16 (1992)

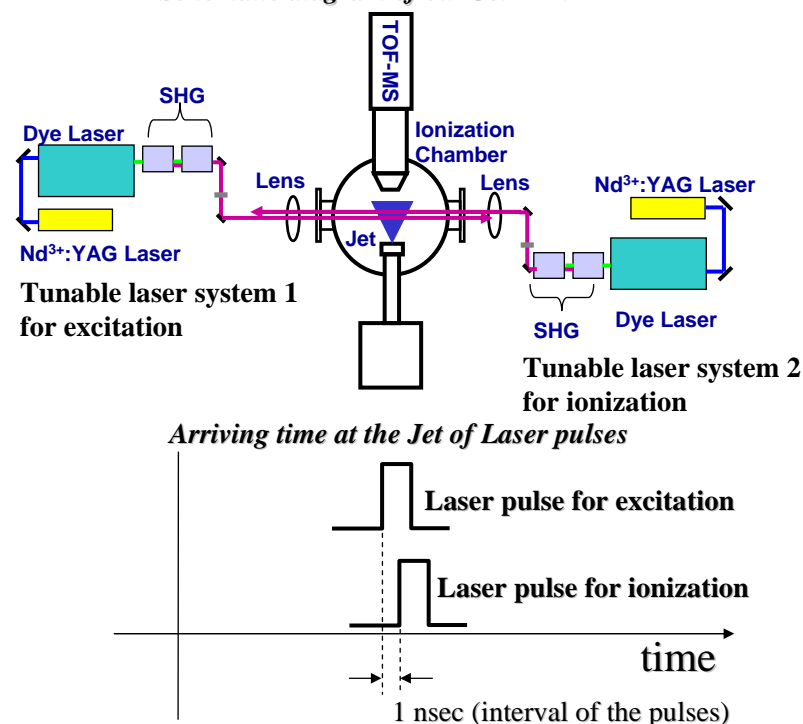
### Apparatus



### In case of PAHs

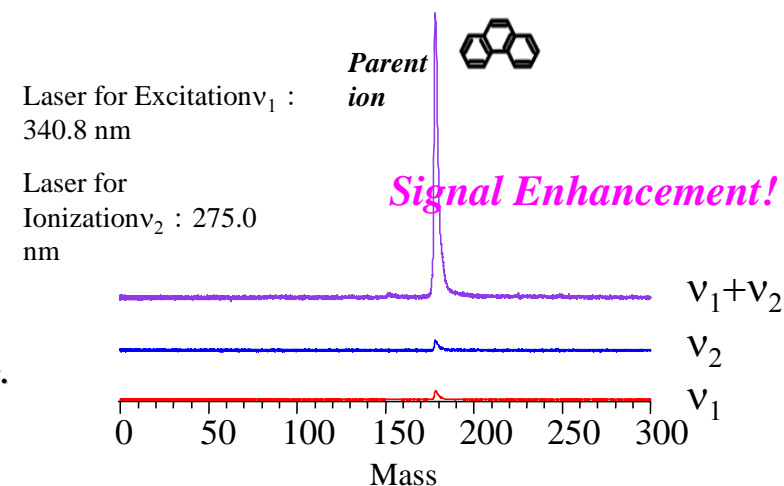
We must use 2 different kinds of tunable lasers for the detection of PAHs with isomer selectivity.

### Schematic diagram of our Jet-REMPI

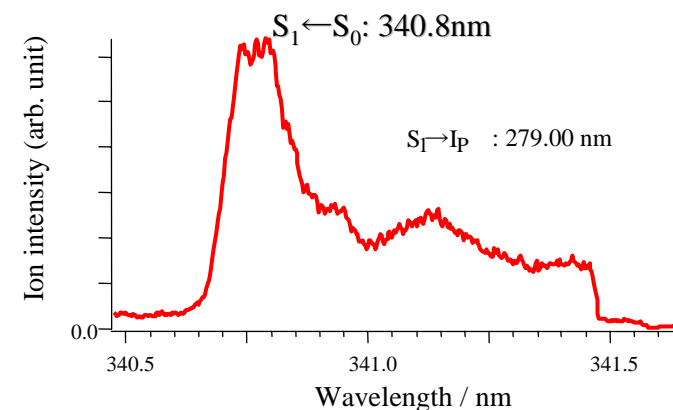


### Results

### REMPI Mass Spectra of Phenanthrene



### REMPI spectrum of Phenanthrene

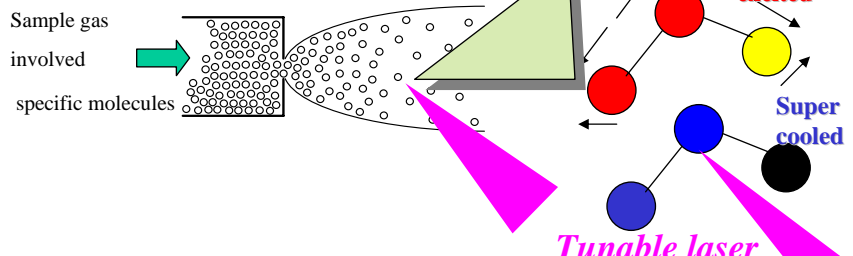


# Principle of Jet-REMPI

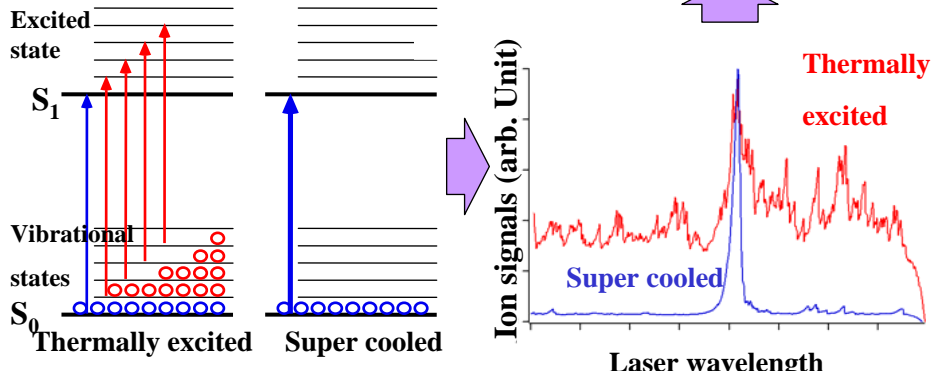
Supersonic Jet-Resonance Enhanced Multi-Photon Ionization

## Supersonic Jet

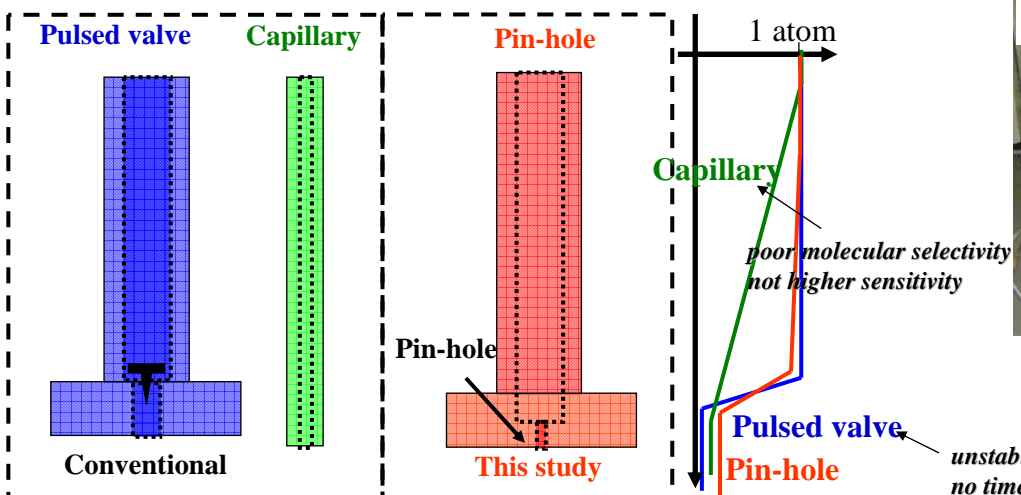
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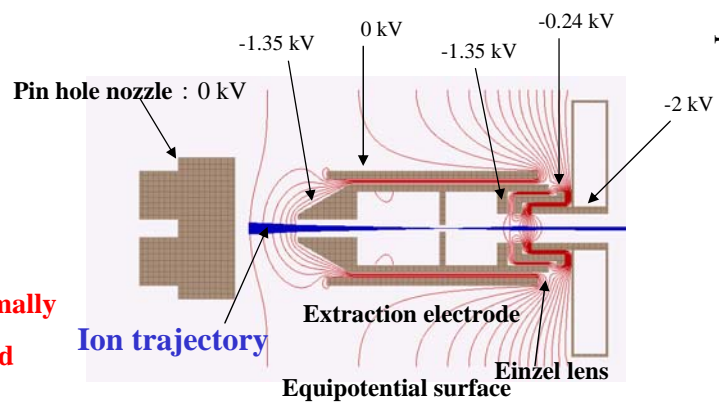
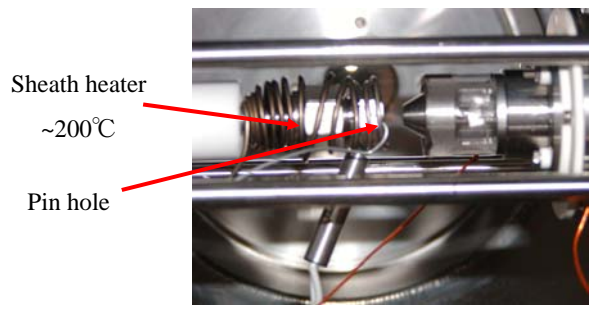
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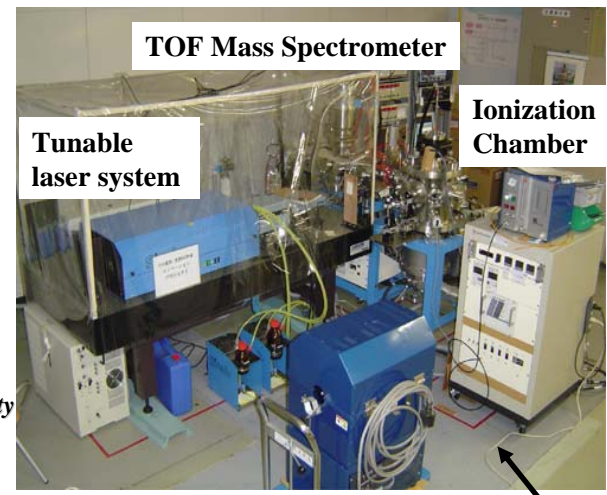
Adiabatic expansion efficiency:  $(T/T_0) = (P/P_0)^{(\gamma-1)/\gamma}$



## Sample introduction through the pin hole with heating



Photograph of our Jet-REMPI



## Calibration curve of phenanthrene taken by REMPI

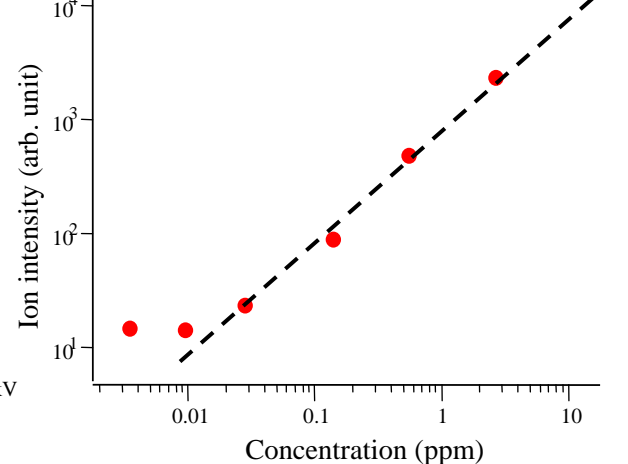


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