

Infrared Analysis of Thin Multilayered Polymer Film Using Cantilever Enhanced Photoacoustic Detector

Kaori Watanabe and Fumiko Hiwatashi



Systems Engineering Inc. www.systems-eng.co.jp info@systems-eng.co.jp

Introduction

Polymer thin film is used in...

- Structural material
- Electronic device
- Adhesive
- Paint and printing
- Biomaterial

nm to μm ordered polymer structure

Multilayered films for hybrid and novel functions

Depth profiling analysis is necessary

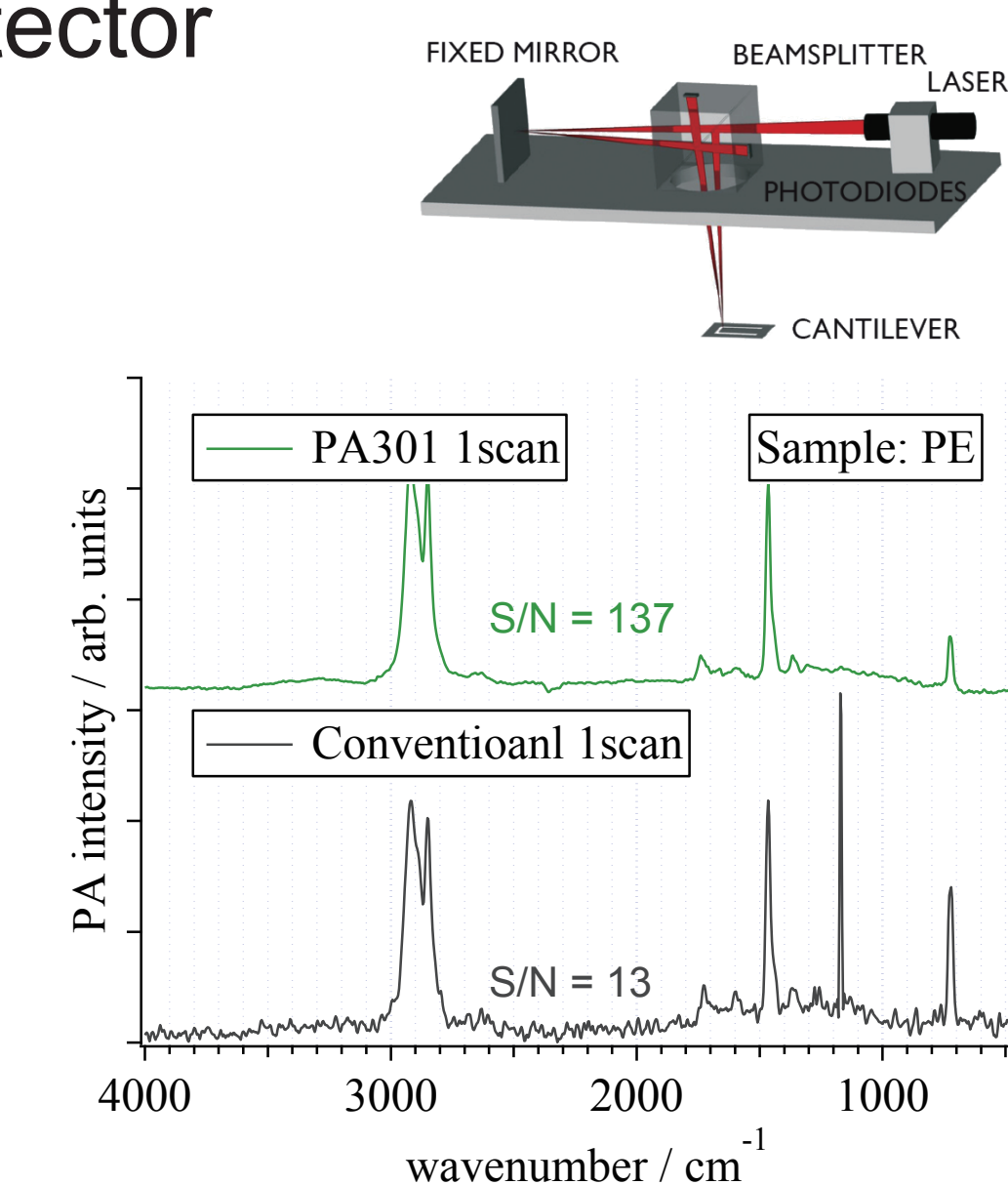
Surface analysis

- XPS, SSIMS, SPM, XRD etc.
- Vibrational spectroscopy -> definitive molecular information
 - » PAS: Non-destructive (little sample preparation), depth-profiling

Novel PAS detector (GASERA; booth 555)



- Cantilever and laser interferometer based detector
- **Ten times more sensitive than traditional acoustic microphone**



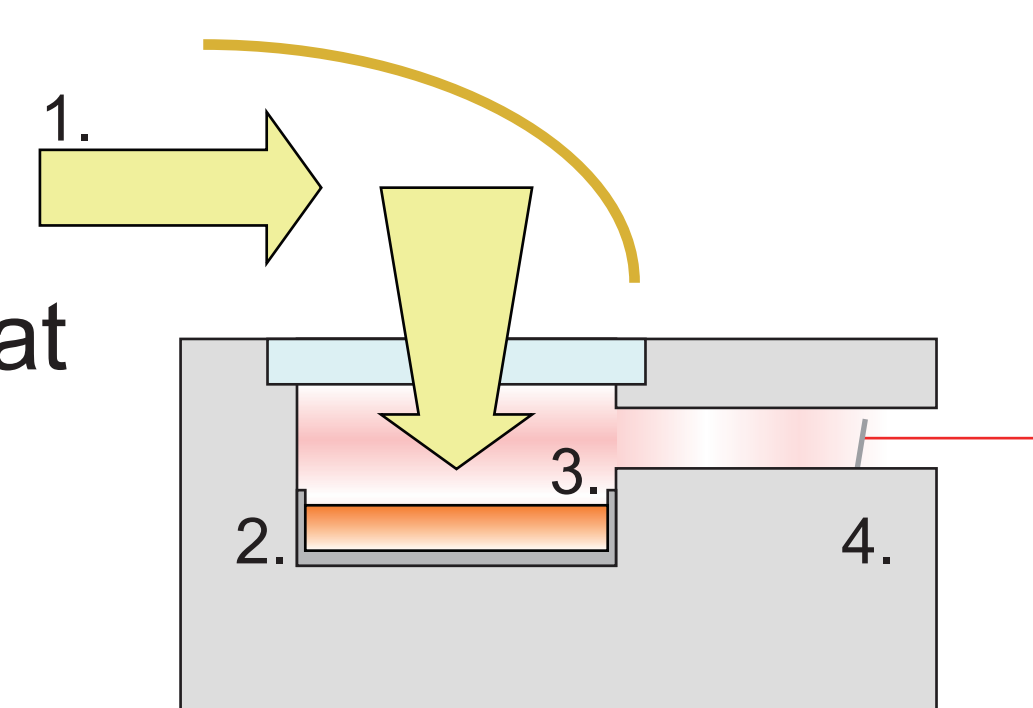
This study

- Infrared PAS analysis of multilayered films
- Determination of accurate sampling depth of PAS with cantilever detector

Photoacoustic Spectroscopy (PAS)

Photoacoustic spectroscopy

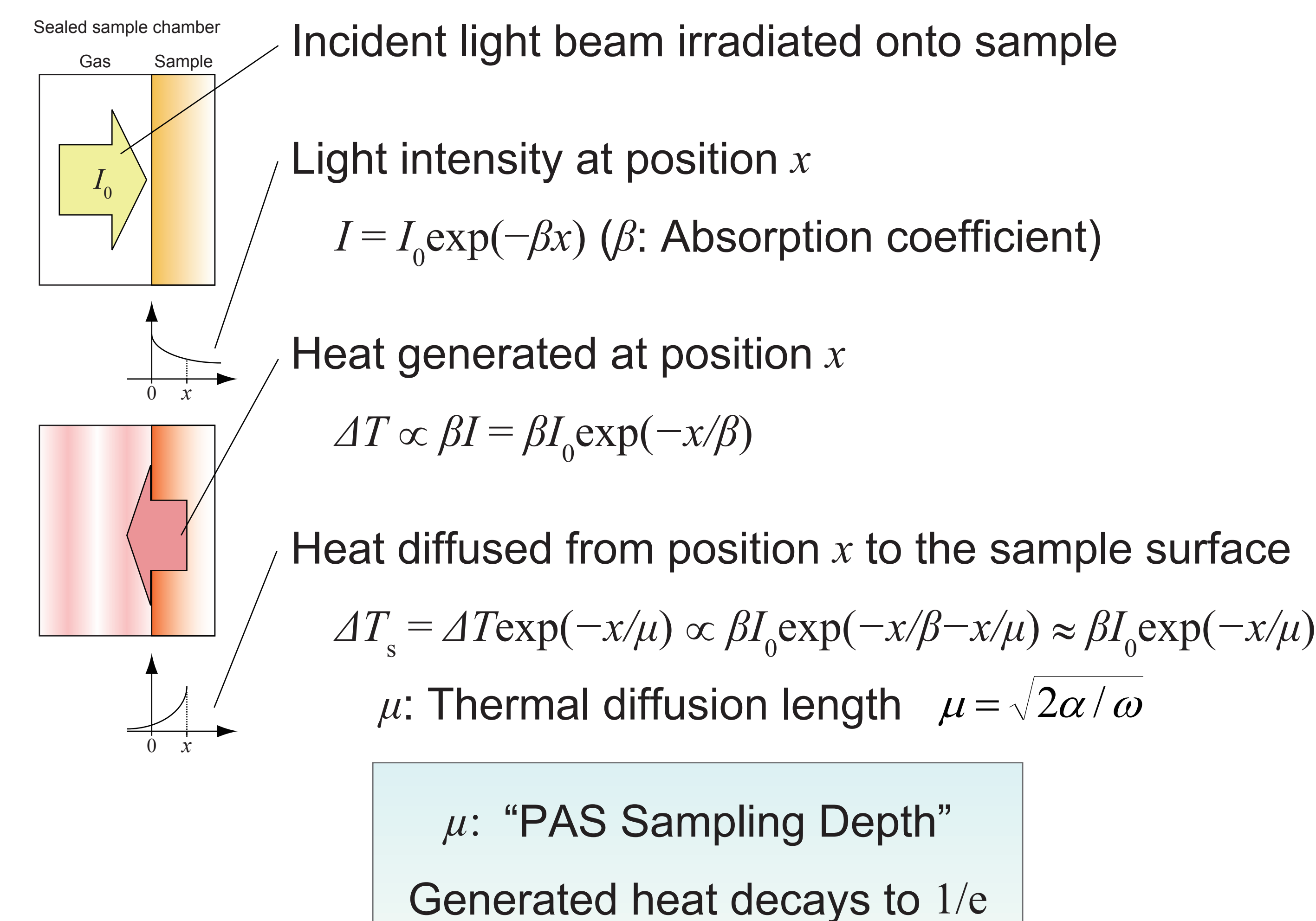
1. Sample absorbs incident light
2. Absorbed energy partially transformed into heat (non-radiating relaxation)
3. Heat diffuses back to sample surface
4. Thermal expansion of surrounding gas detected



PAS advantage

- Highly sensitive
- Non-destructive
- Depth-profiling
- Versatile
 - » Irregular shaped, small, or opaque sample etc.
 - » THz, IR, NIR, UV-Vis etc.

PAS Sampling Depth



α : Thermal diffusivity $\alpha = k/\rho C$ [$\text{cm}^2 \text{s}^{-1}$] ω : Angular modulation frequency $\omega = 2\pi V\nu$

k : Thermal conductivity [$\text{W cm}^{-1} \text{K}^{-1}$] V : Mirror velocity [cm s^{-1}]

ρ : Density [kg cm^{-3}] ν : Infrared wavenumber [cm^{-1}]

C : Specific heat [$\text{J kg}^{-1} \text{K}^{-1}$]

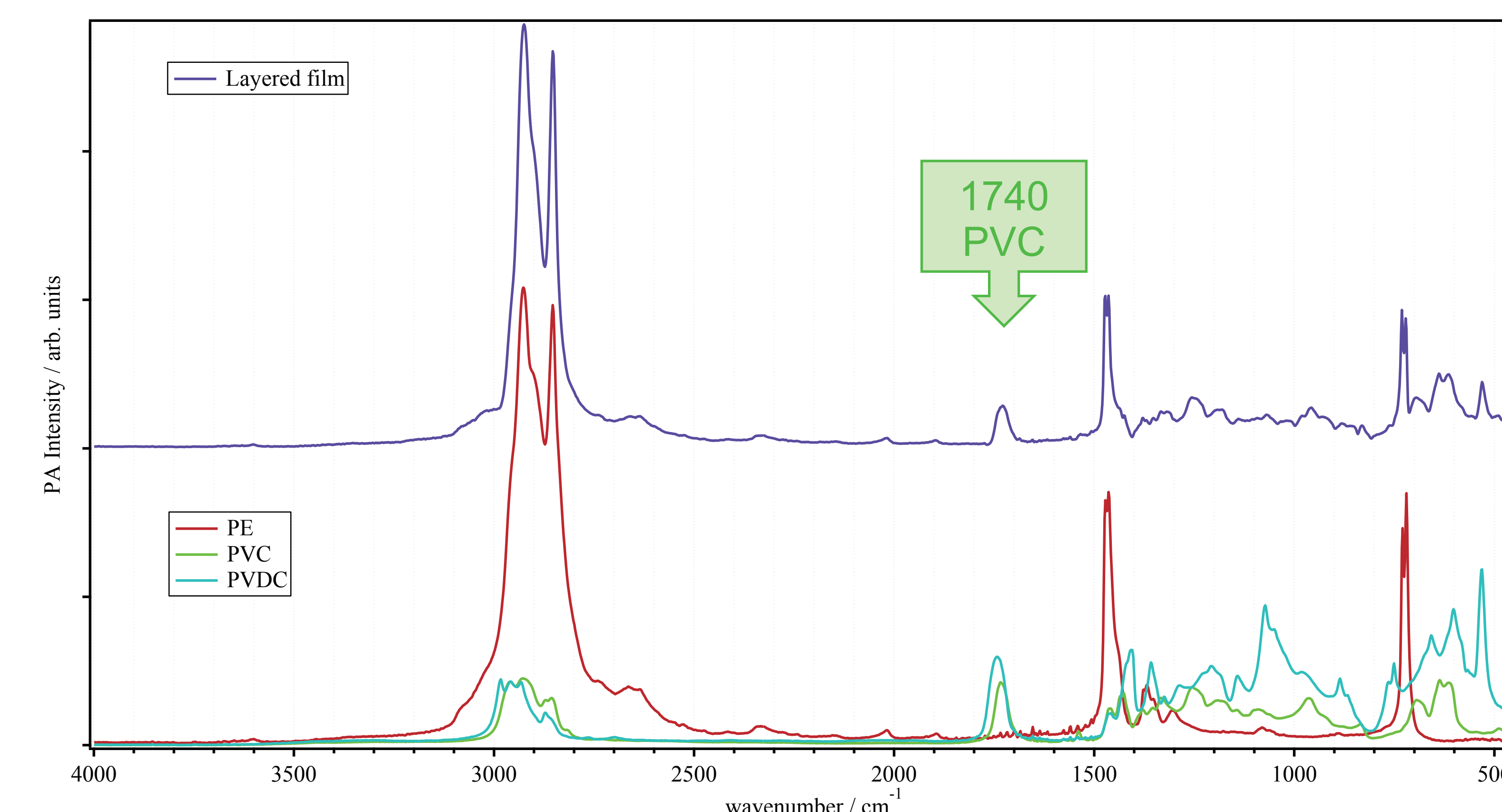
Results and Discussion

1. PAS spectrum of multilayered film

Layered sheets of food wrap

PE, PVC, PVDC; 10 μm each

Mirror velocity $V = 5 \text{ kHz} = 0.32 \text{ cm s}^{-1}$



1740 cm^{-1} peak of PVC observed

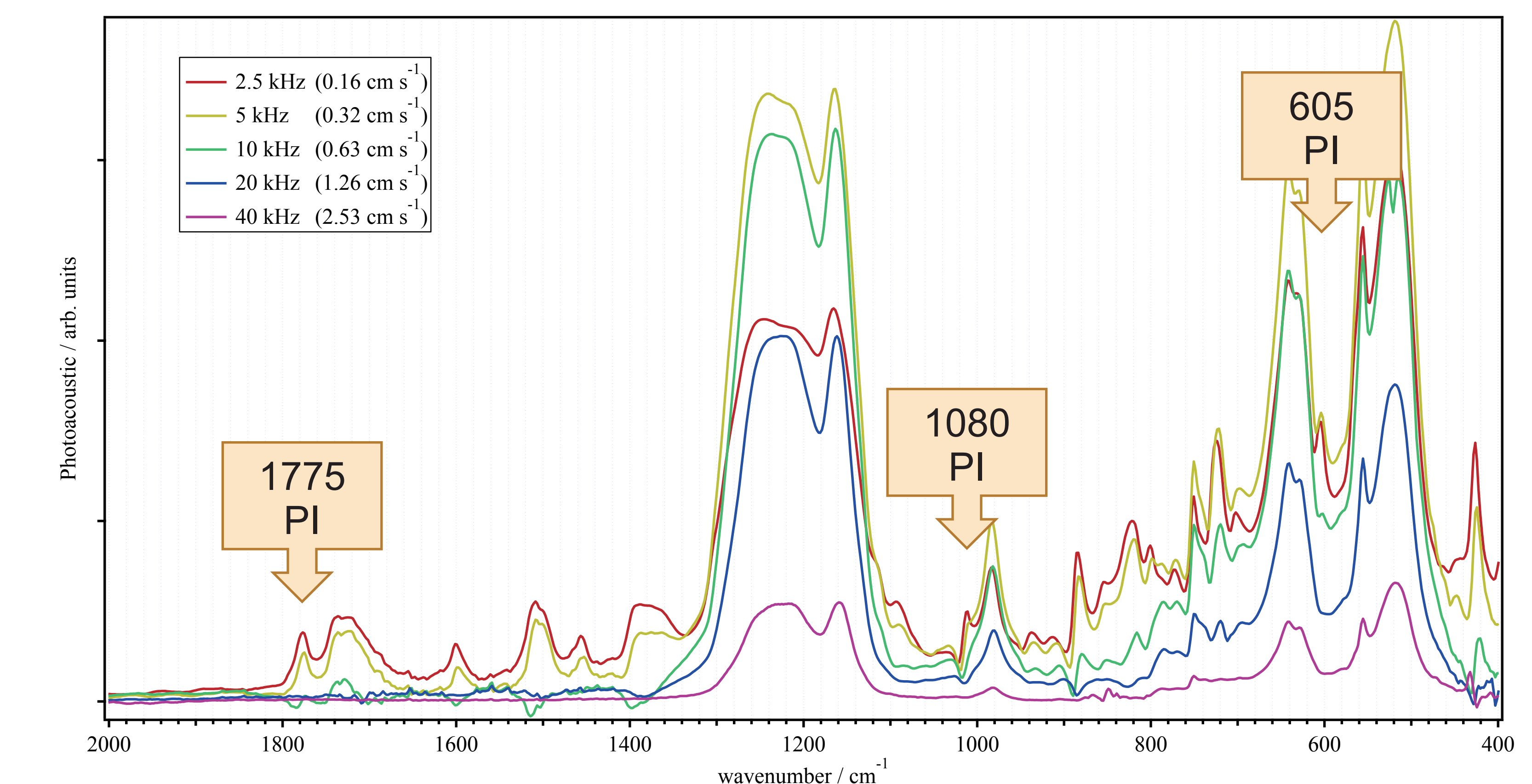
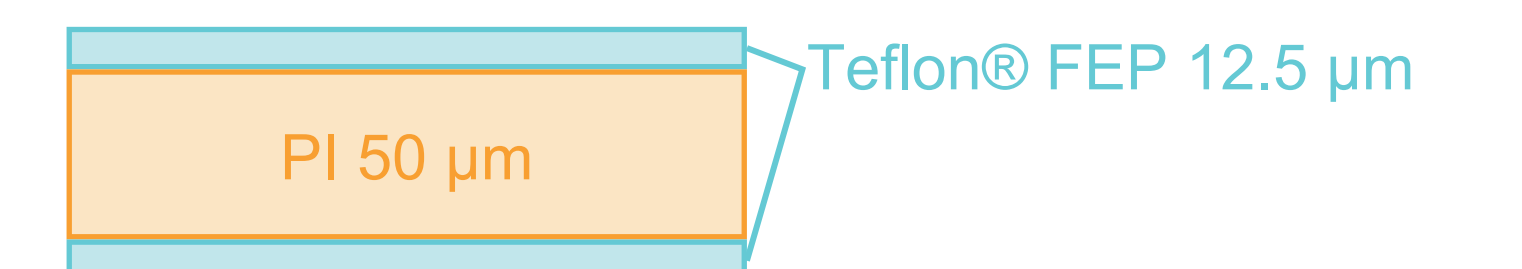
Sampling depth $> 10 \mu\text{m}$ $\leftrightarrow$ PAS sampling depth $\mu = 7.6 \mu\text{m}$

Photoacoustic signal observed beyond μ

2. PAS spectrum of multilayered film, various mirror velocity

Multilayered polyimide film

Kapton® 300F929



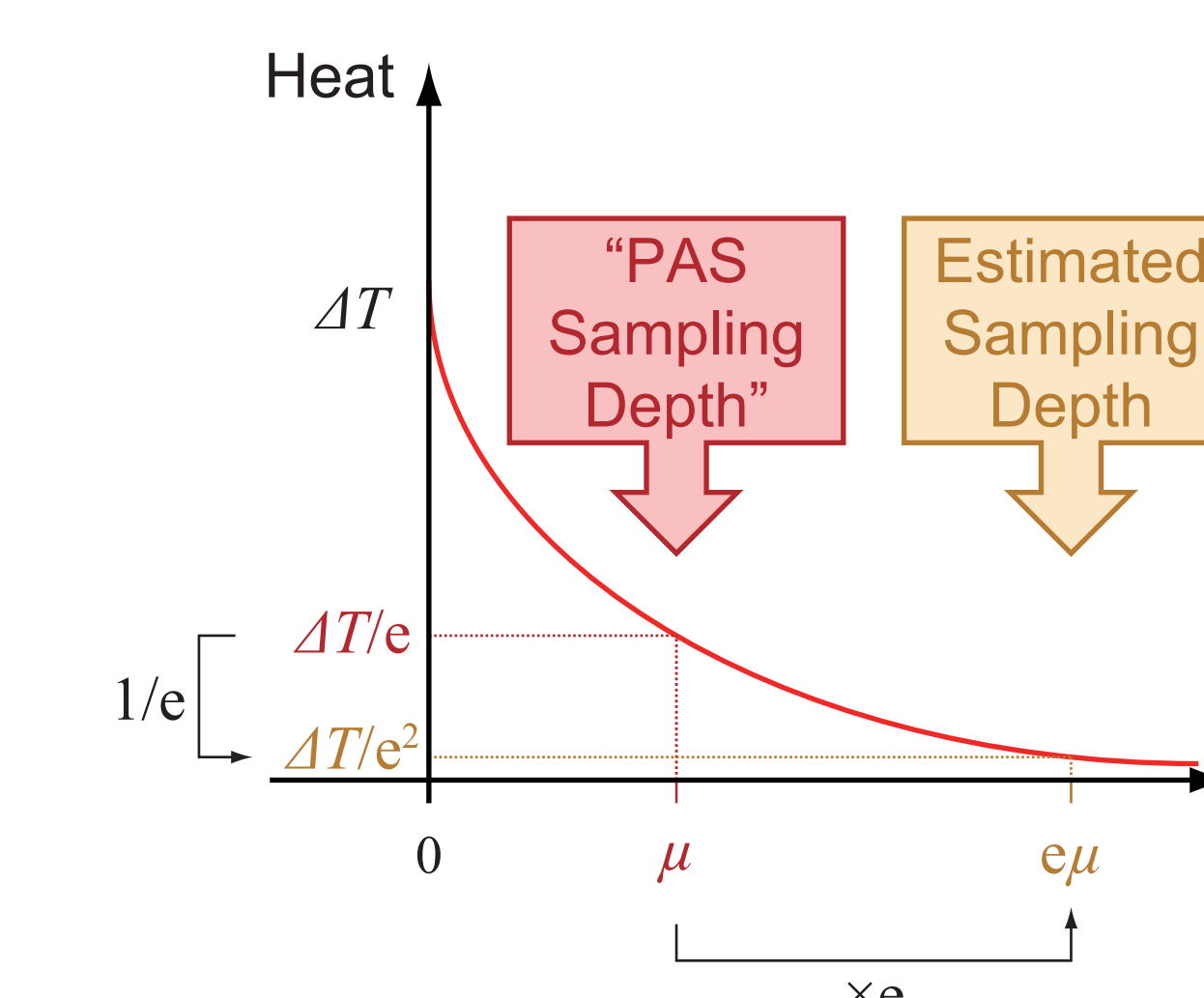
Estimation of accurate sampling depth $A\mu$ (A : factor)

- 1775 cm^{-1} peak: Observed at 10 kHz, not observed at 20 kHz
 - » $3.8A < 12.5 \mu\text{m} < 5.3A$
- 1080 cm^{-1} peak: Observed at 10 kHz, not observed at 20 kHz
 - » $3.4A < 12.5 \mu\text{m} < 4.8A$
- 605 cm^{-1} peak: Observed at 20 kHz, not observed at 40 kHz
 - » $4.6A < 12.5 \mu\text{m} < 6.4A$

Estimated factor

$2.6 < A < 2.7$

i.e., $A \approx e$



Heat generated at depth $e\mu$ can be detected

Generated heat decays to $1/e^2$ at surface

Conclusion

Photoacoustic signal can be detected beyond PAS sampling depth μ .

Accurate sampling depth is estimated to be $\sim e\mu$, where the generated signal decays to $1/e^2$ upon reaching the sample surface.