On the feasibility of the Radiochromic film dosimetry using Raman-spectroscopy based on the change of carbon triple bonds concentration

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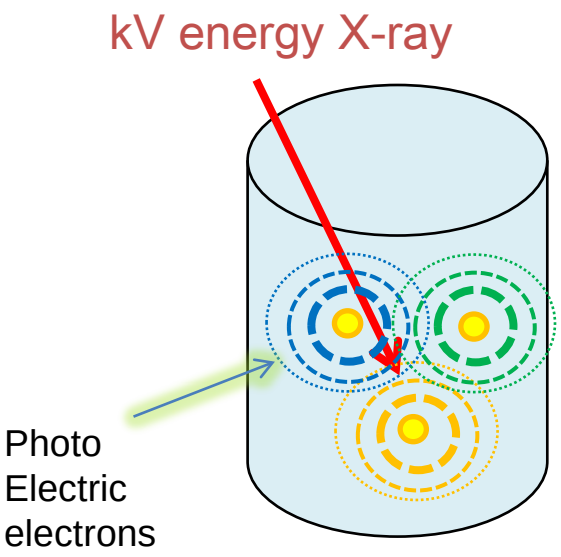
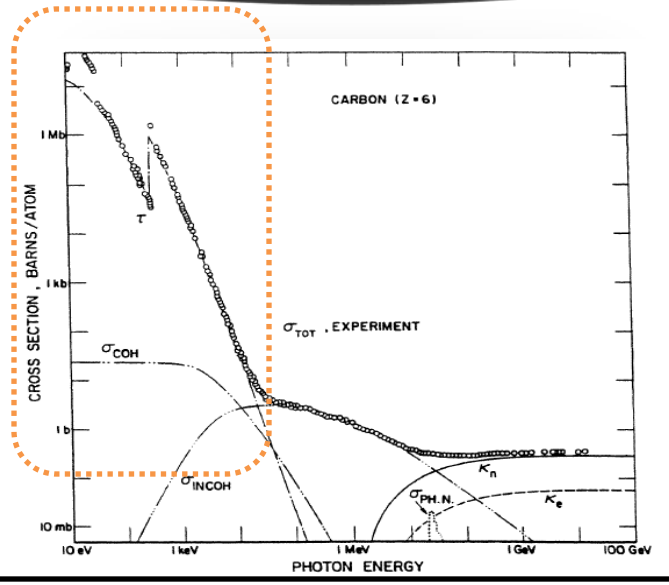
Localized Dose Enhancement

- High-atomic-number(Z) : gold nanoparticles(AuNPs)

: proven to enhance radiation effects in kilovoltage x-ray radiation therapy beams(*)



$$\sigma_{tot} = \sigma_{pe} + \sigma_{incoh} + \sigma_{coh} + \sigma_{pair} + \sigma_{trip} + \sigma_{ph.n}$$



Photon cross section data ranging from 10eV to 100GeV-J H Hubbell

* W. N. Rahman et al. Nanomedicine: Natotechnology, Biology and Medicine, Vol,5, p. 136-142, 200

Localized Dose Enhancement

kV energy-dorminant **photoelectric cross section** based on NIST data

$\sigma \times \rho_N$ Is proportinal to

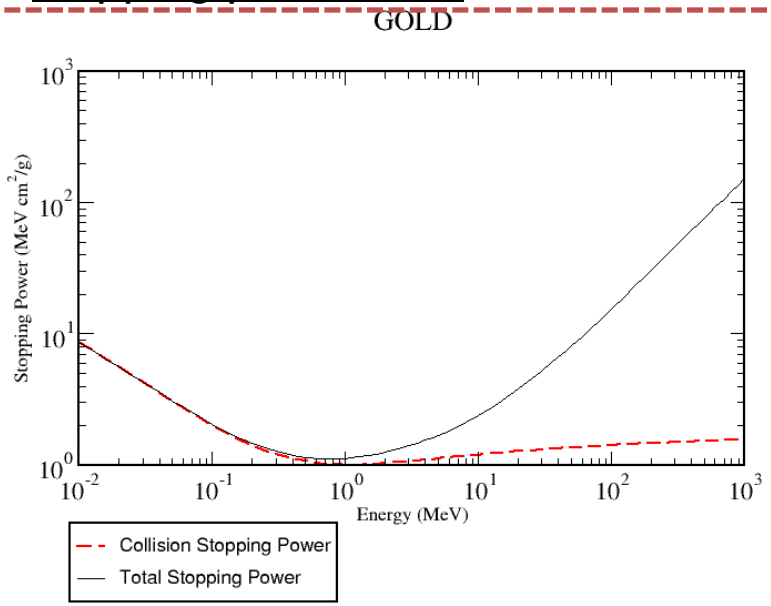
absorbed energy in a specific material irradiated by some energy photon

① Gold concentration is 0.55 mmol ; ratio of Au and water molecules number density = 1 : 10^{-5}

② 3% energy absorption is estimated to increase when 30kV source used

• Auger electrons : deposited within only nano meters

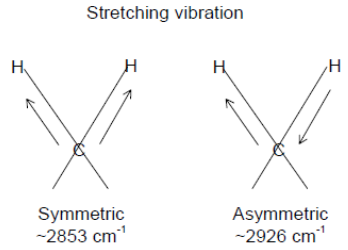
• kV photoelectrons : several decades micro meters by stopping power data.



Stopping power of Gold(NIST)

Raman Spectroscopy

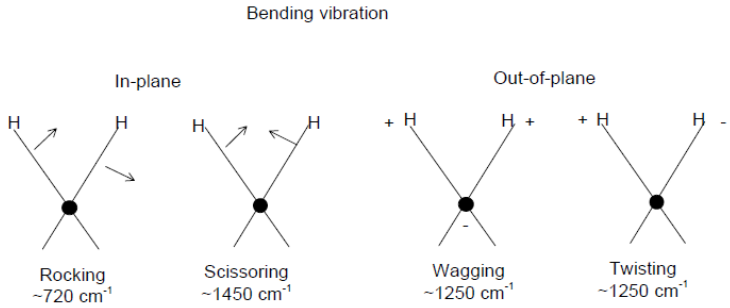
- Common vibrational spectroscopies for assessing **molecular motion** and **fingerprinting species**



- Transmittance after absorption

incidence → ? → **scattered**

- Only possible if the **dipole moment** of the molecule changes as a result of molecular vibration



Example of molecular vibration mode for CH_2

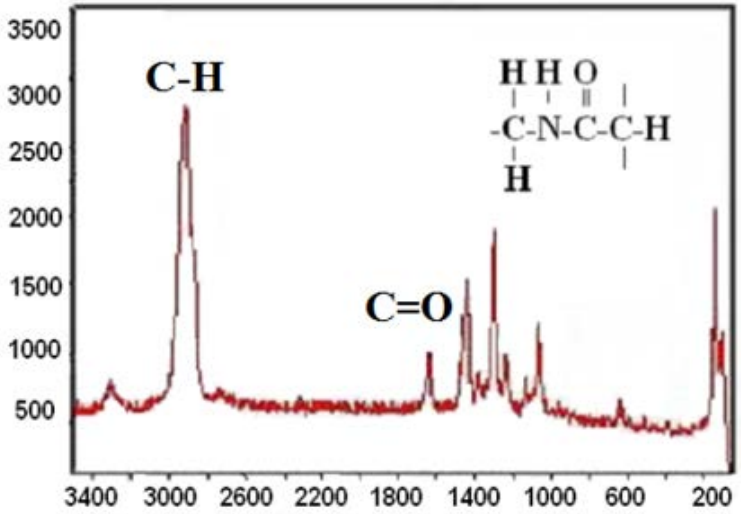
Wavelength shift = inherent vibration energy

- Based on inelastic scattering of a monochromatic excitation source

- Routine energy range:

  200 - 4000 [1/cm]

- The wavelength shift of scattered light is not affected by incident light wavelength



Raman phenomenon

Classical theory of Electromagnetism states

Peak's intensity

$$I = \frac{\nu_0^4}{12\pi\varepsilon_0 c^3}\left|p\right|^2$$

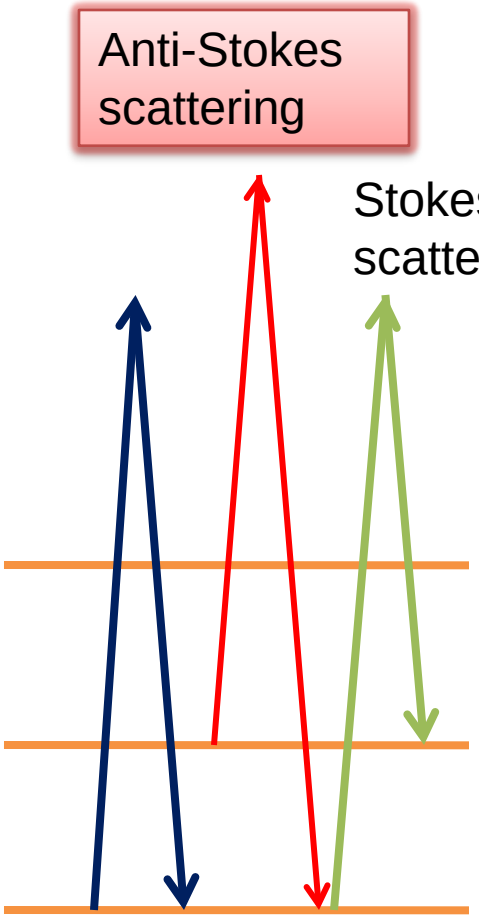
Where the induced dipole moment is…

$$p = \alpha_0 E_0 \cos(\nu_0 t) + \sum_{k=1}^{n} \alpha_k E_0 \cos(\nu_0 t)\cos(\nu_k + \phi_k)$$

When Dipole moment depends on the polarizability of the molecule
Such that $\mu = \alpha E_0 \cos(\nu_0 t)$

Varies with every vibrational motion of molecules!

Raman scattered



In the Quantum mechanical model,

The intensity depends on the occupation of the initial state : Boltzmann distribution

The intensity ratio is…

$$\frac{I(Stokes)}{I(anti-Stokes)} = \frac{(\nu_0 - \nu_k)^4}{(\nu_0 + \nu_k)^4} e^{-hc\nu_k / kT}$$

Why Raman as dosimeters?

1) Most Sensitive Spectroscopy

- Scatterd : Only one photon of $10^3 - 10^4$
- Only one of a 1,000 or 10,000 scattered photons have modulated frequency
- The intensity of Raman signal is a millionth of the incident of the incident light

- Confocal Raman microscope
- The modern techniques : resonance Raman and SERS : turned Raman spectroscopy to a sensitive method

2) Strong signals for

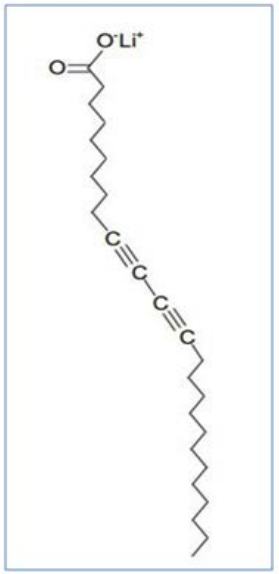
- Strong for carbons
- Symmetric molecular vibrational modes

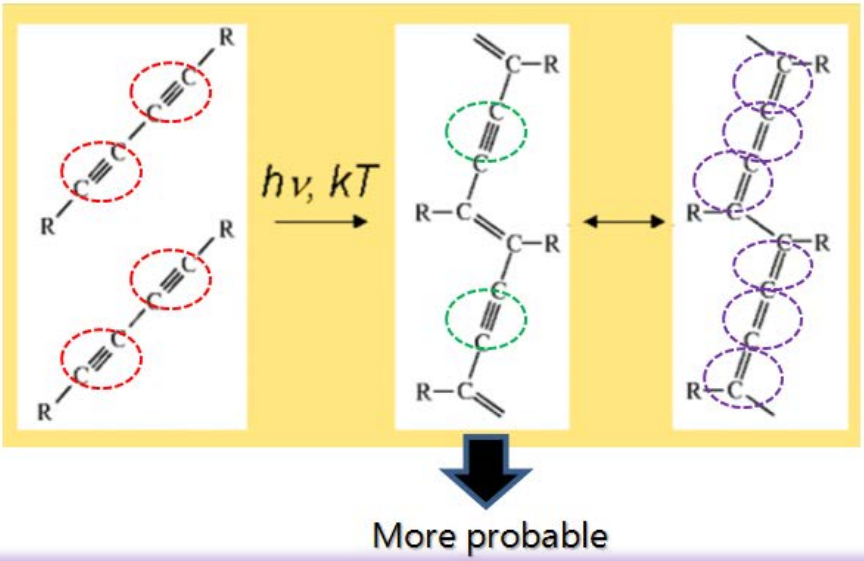
3) Raman's peak is proportional to

✓ Electric field(laser)'s intensity

✓ Concentration of molecules

Newly found Radiochromic Films Features



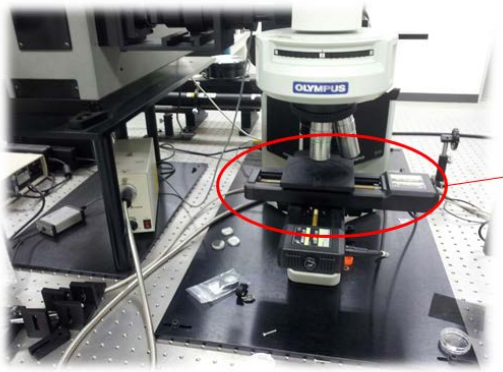


The polymerization schematic ; \
by courtesy of
D.F. Lewis,
Ph.D ,Ashland Co.

What else if irradiated?

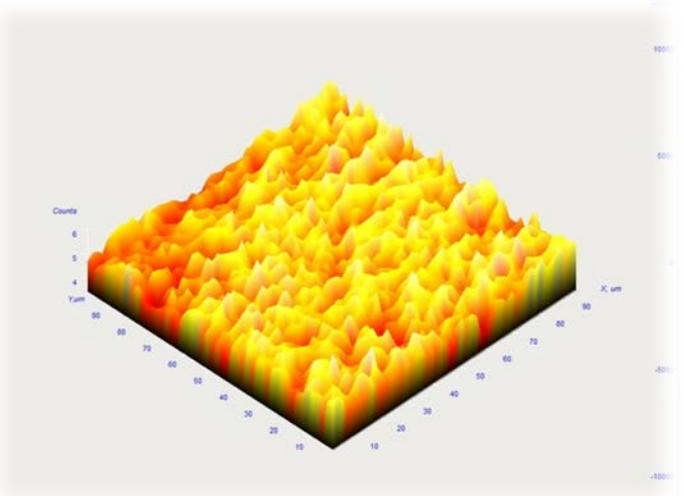
1. Polymerization Cross-linking
2. The number of Carbon triple bonds belong to monomers decrease, synchronizing with polymer's increase
3. Carbon triple bonds of polymers have more red-shifted wave number than monomers once they are polymerized
4. Newly-produced carbon double bonds

Raman Spectroscope & Films

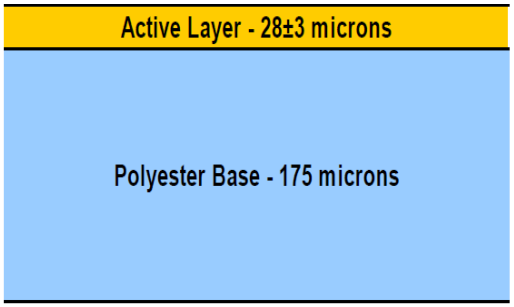


2차원 scan 가능한
Motor stage

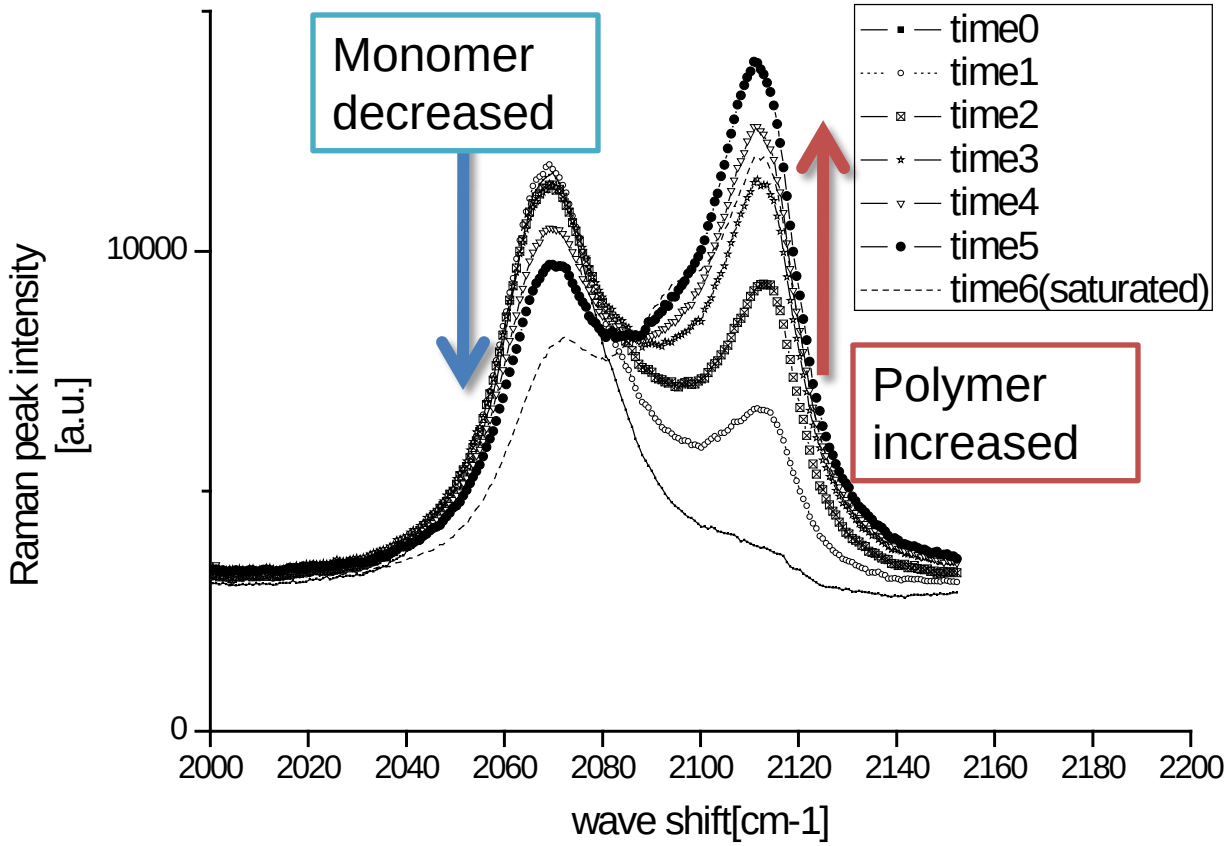
서울대 융합과학기술원 라만 분광기



Actual Raman data acquisition by 2D scanning of irradiated radiochromic films
: by courtesy of Lambda Ray Co., Ltd.
Nanofinder FLEX G model used for measurement

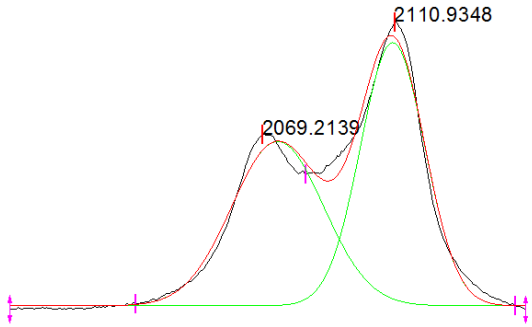


Raman peak change by time : Laser Effect



50MU delivered film analyzed as time changes. This data was acquired within five minutes. The concentration of triple bond for cross-linked polymers increases. Time0=5 seconds exposure, time1=15 seconds exposure, time2=30 seconds exposure, time3 =40 secodns exposure, time4=50 seconds exposure, time5=1minute exposure, time6=3minutes exposure(peak intensity was al most saturated)

Laser effect analysis

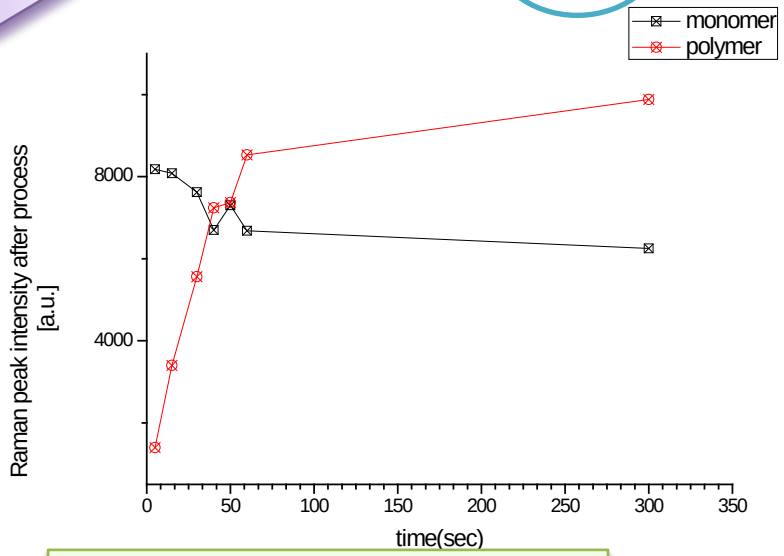


1. Remove fluorescence (background signal)

2. Separate overlapped peaks

Focused laser produces a drastic increase of Raman cross section

Exposing Time	Momomer peak(a.u.) for 2070cm^{-1}	Polymer Peak(a.u.) for 2110 cm^{-1}
Time 0	8180	1400
Time 1	8080	3400
Time 2	7620	5560
Time 3	6700	7240
Time 4	7300	7370
Time 5	6680	8530
Tiem 6	6250	9880



Could be a dose map!!

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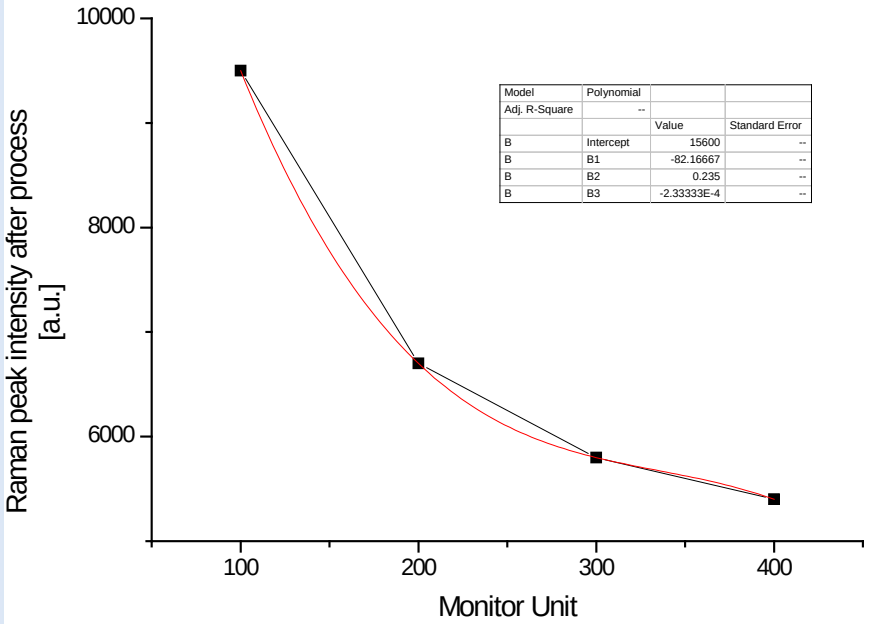
Dose Linearity for monomers



- Decreasing trend for film samples ranging from 100MU to 400MU
- Only one trend was observed; monomer's peak decreases
- Wave shift between monomers and polymers is not large

Existing peak of monomers hides the early generation of polymers

(Actually, monomer peaks grow rapidly during the ear ly laser irradiation, affected by the polymer peak's earl y growing, not by the monomer peak's own growing)

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Future work

- Two dimensional Analysis
  - Minimal & Even effect by laser
  - Automatically even exposure
  - Focusing for maximum data acquisition be secured
- Analysis for micro-dosimetry requires…
  - Homogeneously arranged nano-scaled radio-active material : reliable data
  - More sensitive Raman detectors(CCDs)

Conclusion

- Laser Effect should be overcome
- Even Laser exposure within 5secs provide uncertainty and decrease reproducibility of data
- Triple Carbon bonds concentration change due to polymerization by laser focused imply the dose map for arbitrary radiation exposure
- For reliable dosimetry, measurement for more precise and wider range be required

Discussion & Question

Thank you for your attention