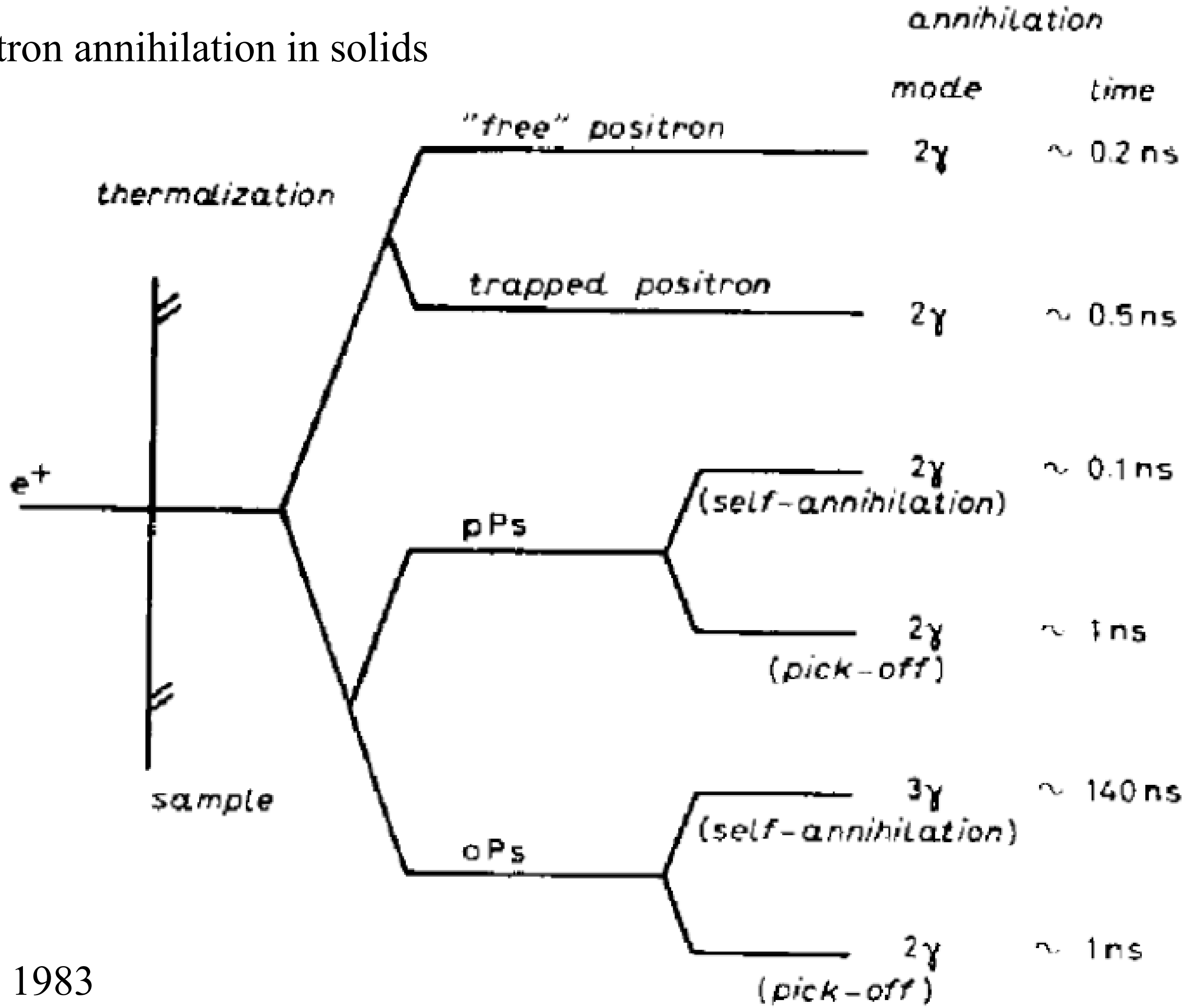
Positronium

• channels for positron annihilation in solids



W. Brandt 1983

Positronium

- **Positronium (Ps)** – hydrogen-like bound state of positron and electron $\Psi_{n,l,m}(\mathbf{r})|S,S_z\rangle$
- singlet state $^1S_0$, **para-positronium (p-Ps)**, antiparallel spins ($S = 0$, $S_z = 0$)
- lifetime in vacuum 125 ps (2γ self-annihilation) $\frac{2\hbar}{m_0 c^2 \alpha^5}$

$$|S=0,S_z=0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle - |\downarrow\rangle|\uparrow\rangle),$$

- triplet state $^3S_1$, **ortho-positronium (o-Ps)**, parallel spins ($S = 1$, $S_z = -1, 0, 1$)
- lifetime in vacuum 142 ns (3γ self-annihilation) $\frac{\frac{9}{2}h}{2m_0 c^2 \alpha^6 (\pi^2 - 9)}$
- maximum positron lifetime is a solid

$$\tau_{\max}^{-1} = \frac{1}{4}\frac{1}{\tau_{p-Ps}} + \frac{3}{4}\frac{1}{\tau_{o-Ps}}$$

$$|S=1,S_z=1\rangle = |\uparrow\rangle|\uparrow\rangle,$$

$$|S=1,S_z=0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\rangle|\downarrow\rangle + |\downarrow\rangle|\uparrow\rangle),$$

$$|S=1,S_z=-1\rangle = |\downarrow\rangle|\downarrow\rangle,$$

Positronium

- **Positronium (Ps)** – energy levels
- analogical to hydrogen atom, but reduced mass is roughly half of that for hydrogen
- reduced mass Ps: $$\frac{1}{\mu} = \frac{1}{m_{e^-}} + \frac{1}{m_{e^+}} = \frac{2}{m_0}$$
- energy levels Ps: $$E_n = -\frac{1}{n^2}\frac{\mu e^4}{8h^2\varepsilon_0^2} = -\frac{1}{n^2}\frac{m_0}{4\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$

$$e^2 = 4\pi\hbar\alpha\varepsilon_0 c$$

$$E_n = -\frac{1}{n^2}\frac{m_0}{4}\alpha^2 c^2 = -\frac{1}{n^2}\frac{511\times 10^3}{4\times 137^2}\,\text{eV} = -\frac{1}{n^2}6.8\,\text{eV}$$

- ground state Ps: $E_1 = -6.8\,\text{eV}$
- 1. excited state Ps: $E_2 = -1.7\,\text{eV}$
- ’size’ of Ps: ≈ 1Å

Ps formation

- **Ore model**
- Ps is formed in insulators during positron thermalization
- positron energy range $E_i - E_{Ps} < E < E_{ex}$ (Ore gap)
- E_i – ionization energy
- $E_{Ps} = 6.8$ eV – Ps binding energy
- E_{ex} – the lowest exitation energy of electron

- **Spur model**
- during thermalization a positron is followed by a cloud of free electrons released by ionization
- Ps is formed by interaction of positron with an electron from spur

Free volume

• **polymers**

• non ideal packing of macromolecules (i.e. not the closest packing)

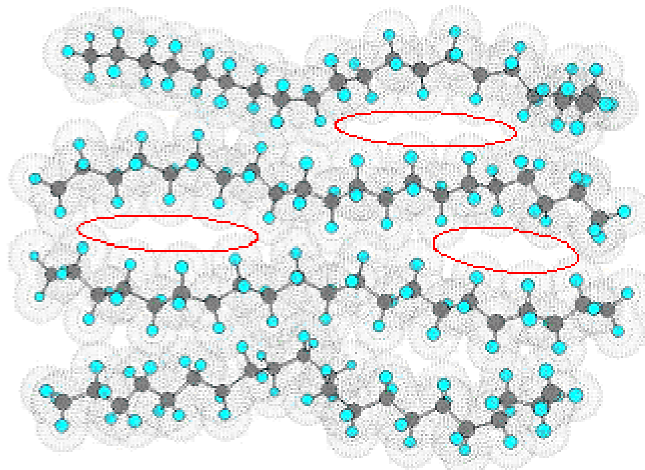
• **free volume**

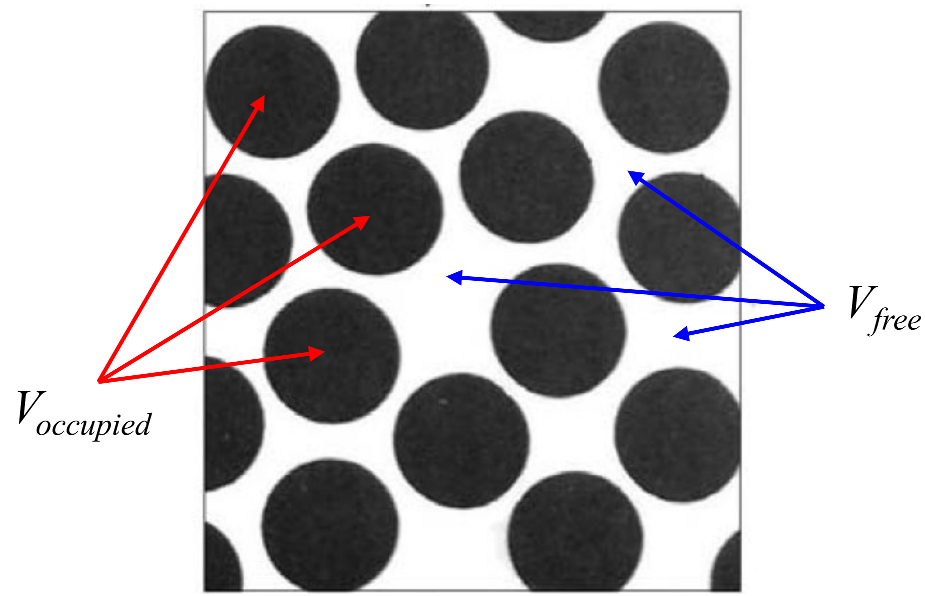
$$V_{free} = V_{total} - V_{occupied}$$

• **fractional free volume**

$$f_V = \frac{V_{free}}{V_{total}}$$

• typical size of free volumes ≈ Å
• relaxation time ≈ 10^{-13} s





Free volume

- **polymers**

- non ideal packing of macromolecules (i.e. not the closest packing)

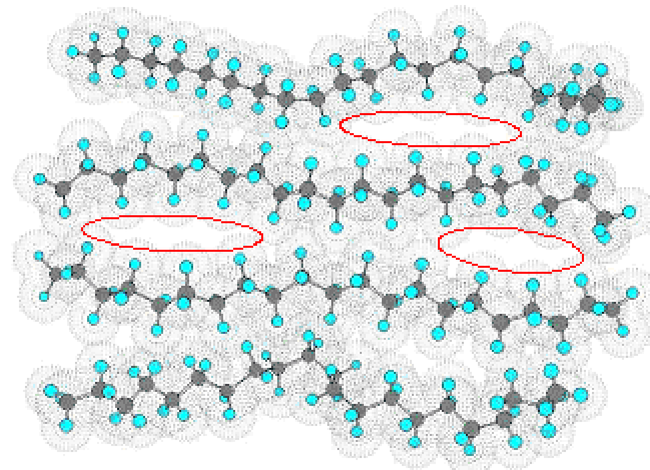
- **free volume**

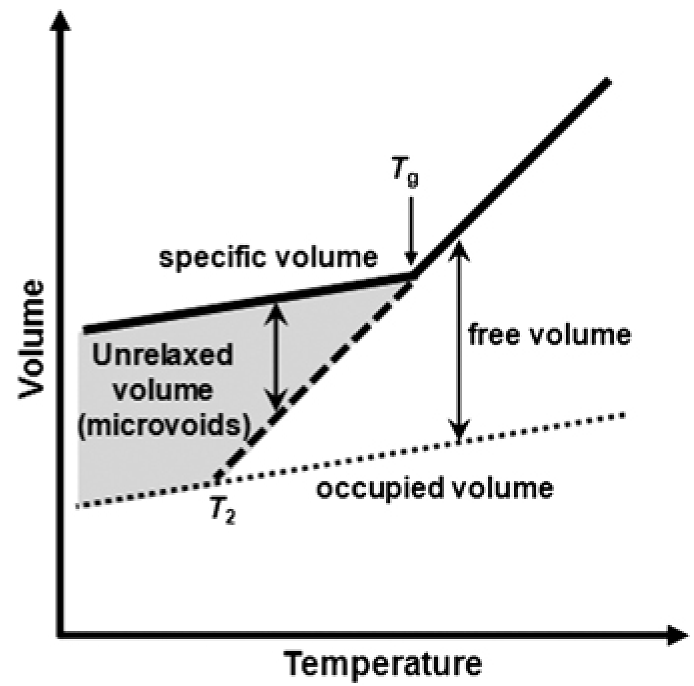
$$V_{free} = V_{total} - V_{occupied}$$

- **fractional free volume**

$$f_V = \frac{V_{free}}{V_{total}}$$

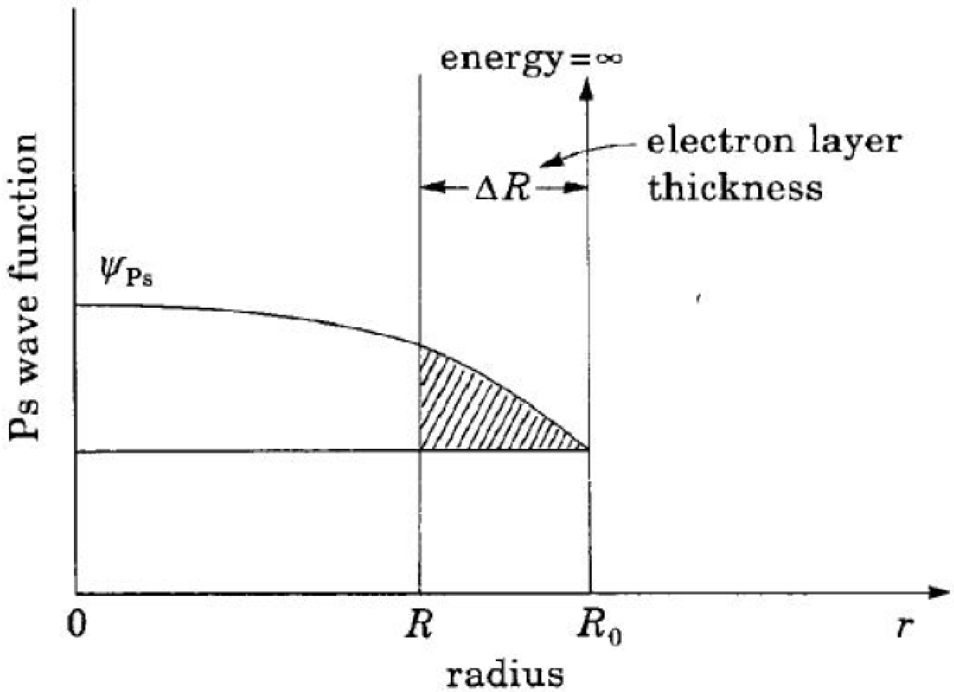
- typical size of free volumes $\approx$ Å
- relaxation time $\approx 10^{-13}$ s





o-Ps pick-off annihilation

- Ps is localized in free volumes
- pick-off annihilation causes significant shortening of o-Ps lifetime



- o-Ps pick-off lifetime in free volume with radius R

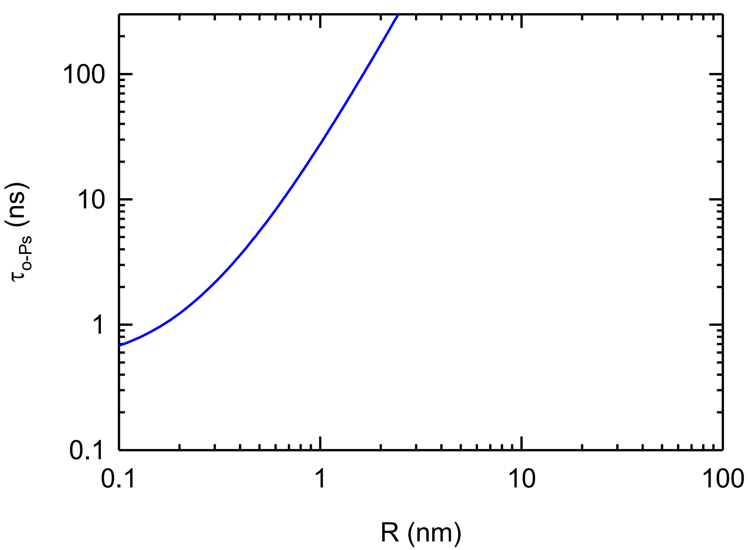
$$\tau_{o-Ps} = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}$$

- $\Delta R = 1.656$ Å

o-Ps pick-off annihilation

• Ps is localized in free volumes

• pick-off annihilation causes significant shortening of o-Ps lifetime



• o-Ps pick-off lifetime in free volume with radius *R*

$$\tau_{o-Ps} = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}$$

• $\Delta R = 1.656$ Å

o-Ps pick-off annihilation

• Ps is localized in free volumes

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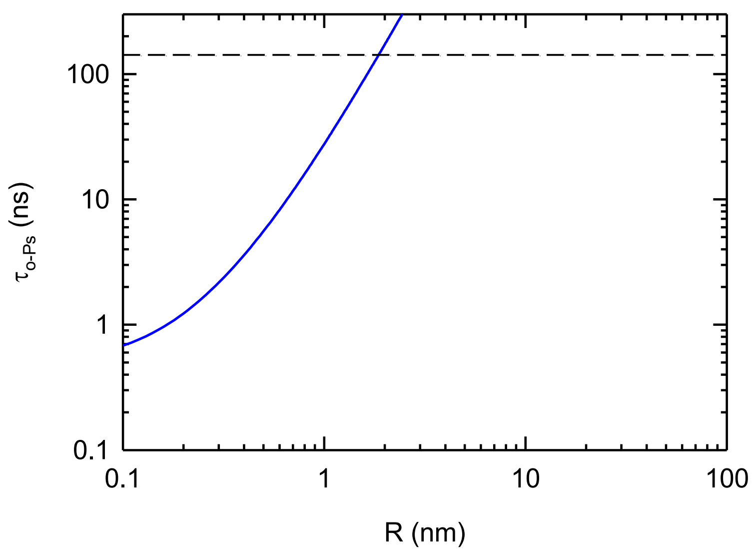

→Lifetime corresponding to o-Ps 3γ self-annihilation:
$\tau_{o\text{-}Ps}$ = 142 ns

• o-Ps pick-off lifetime in free volume with radius *R*

$$\tau_{o-Ps} = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}$$

• ΔR = 1.656 Å

o-Ps pick-off annihilation

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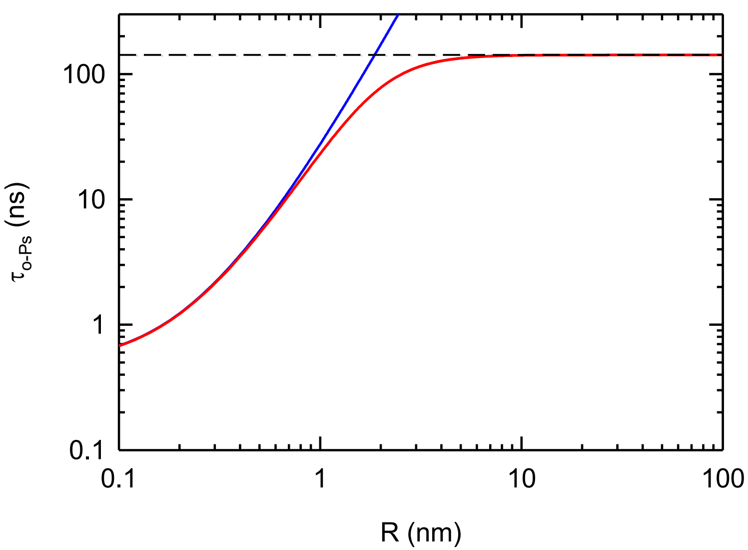


3-γ annihilation included

$$\tau_{o-Ps}^{-1} = \lambda = \lambda_{pickoff}(R) + \lambda_{3-\gamma}$$

$$\lambda_{pickoff}(R) = 2\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]$$

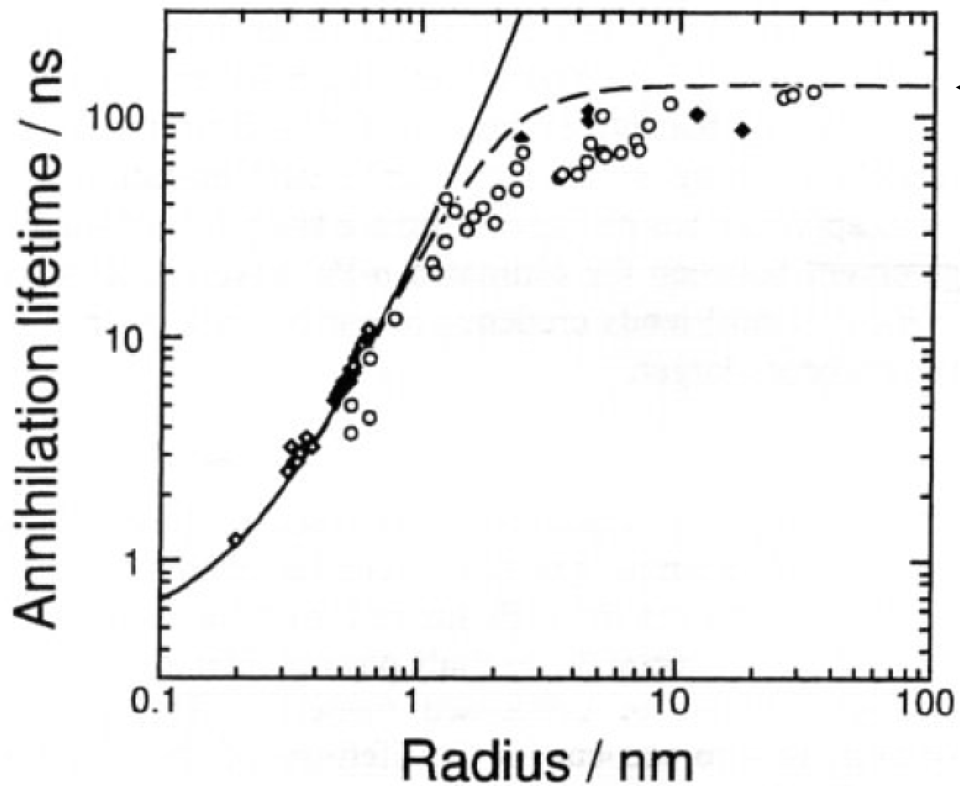
$$\lambda_{3-\gamma} = \frac{1}{142}\ \mathrm{ns}^{-1}$$

$$\Delta R = 1.656\ \text{Å}$$

o-Ps pick-off annihilation

• generalization of Tao-Eldrup model for large pores (Ito 1999)

Tao-Eldrup $$\tau_{o-Ps} = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1}$$



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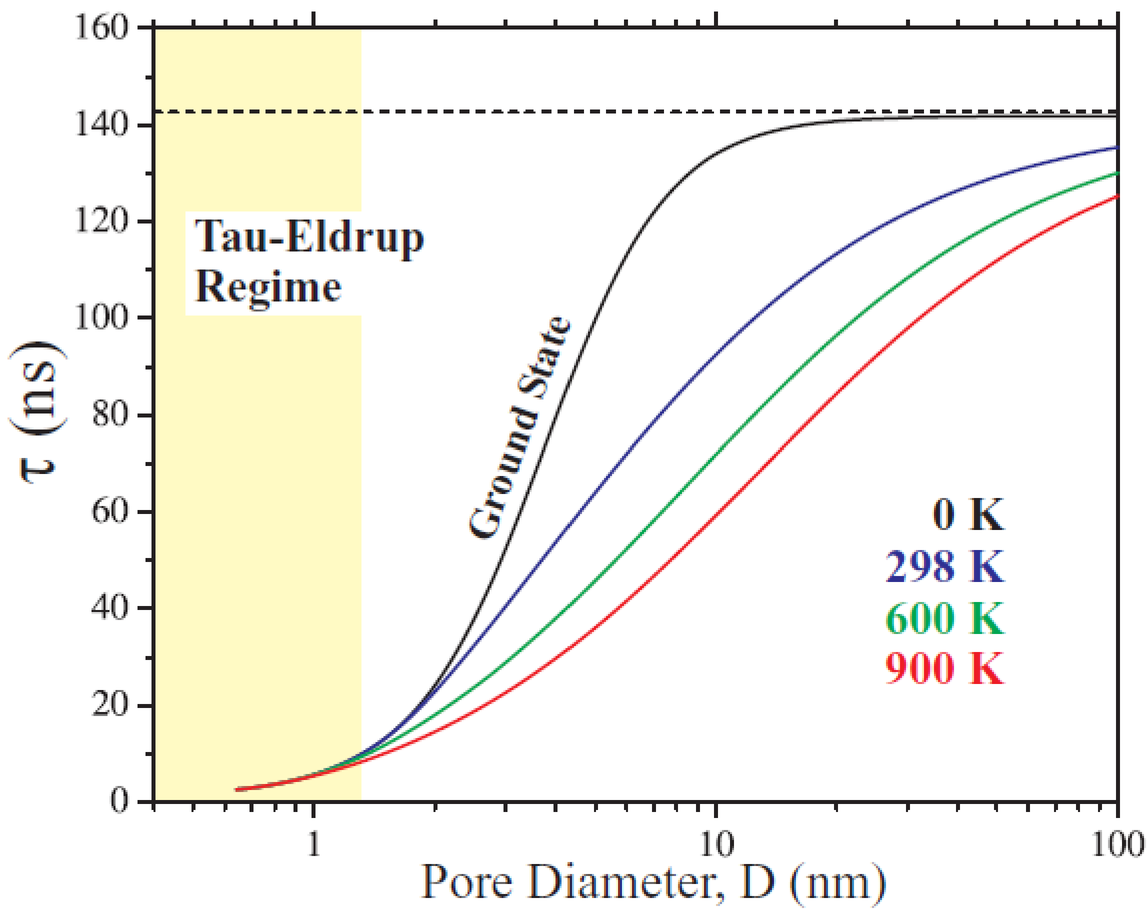
$$\lambda_{3-\gamma} = \frac{1}{142}\ \text{ns}^{-1}$$

$\Delta R = 1.656$ Å

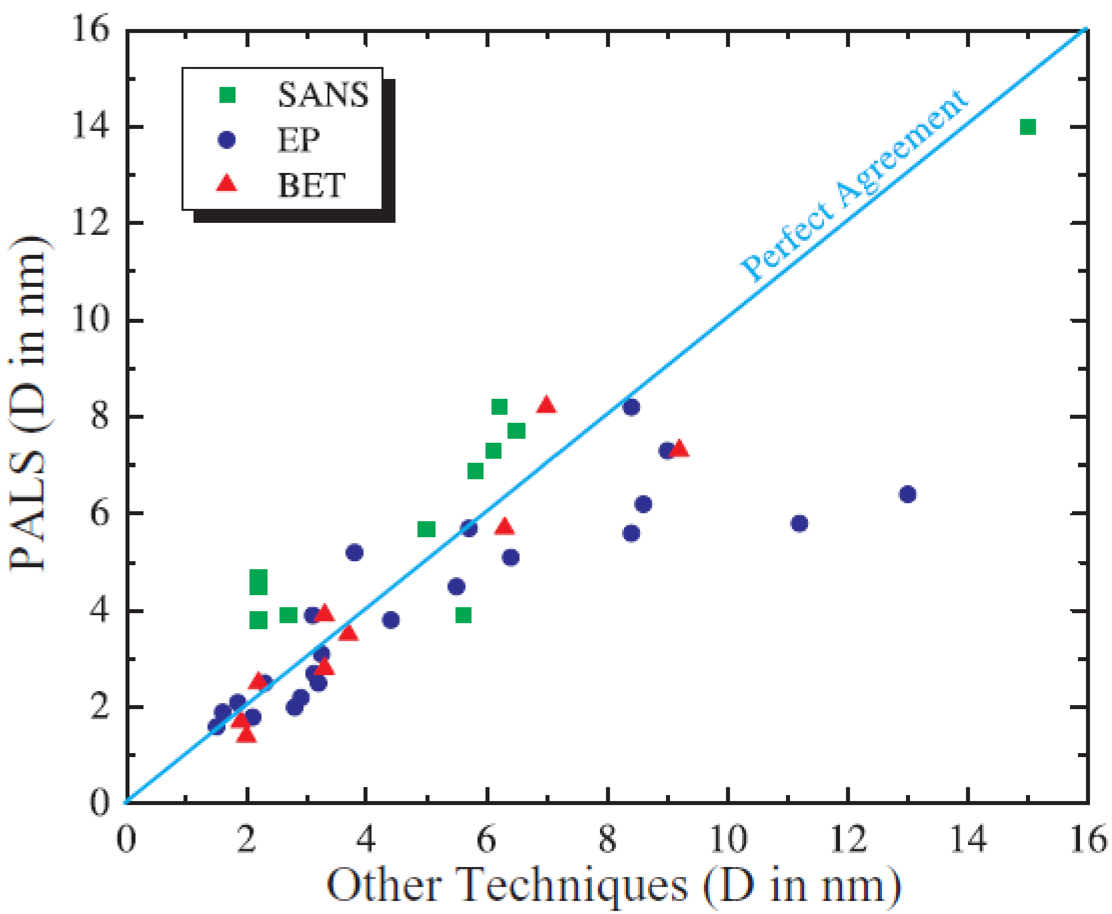
o-Ps pick-off annihilation

• generalization of Tao-Eldrup model for large pores - effect of temperature (Gidley 2006)



o-Ps pick-off annihilation

• comparison of pore size determination using PAS and other techniques



• EP – elipsometrical porosimetry

• BET – gas absorption

• SANS – small angle neutron scattering

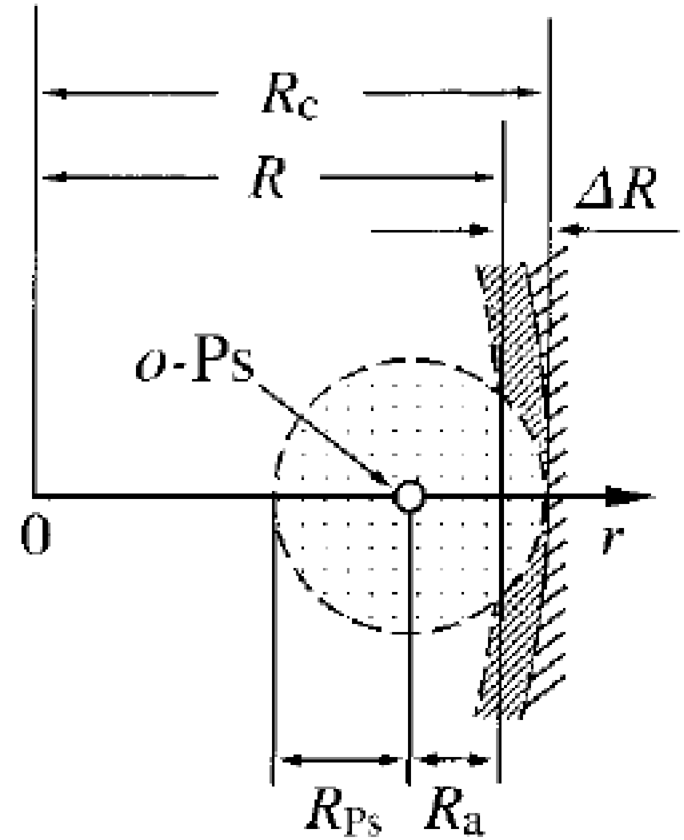
o-Ps pick-off annihilation

- generalization of Tao-Eldrup model for large pores (Ito 1999)
- Ps inside pore $r < R - R_a$

  - no interaction with pore wall: $\lambda_{o-Ps} = \lambda_{3-\gamma} = \frac{1}{142}\ \text{ns}^{-1}$

- Ps close to wall $R - R_a < r < R + \Delta R$

  - Ps interaction with pore wall: $\lambda_{o-Ps} = \lambda_{pickoff}(R) + \lambda_{3-\gamma}$



$$\lambda_{pickoff} = 2\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]$$

$$\lambda_{o-Ps} = \left(1 - f(R)\right)\left(\lambda_{pickoff}(R) + \lambda_{3-\gamma}\right) + f(R)\lambda_{3-\gamma}$$

$$\lambda_{o-Ps} = \left(1 - f(R)\right)\left(\lambda_{pickoff}(R)\right) + \lambda_{3-\gamma}$$

o-Ps pick-off annihilation

- generalization of Tao-Eldrup model for large pores (Ito 1999)

$$\lambda_{o-Ps} = (1 - f(R))(\lambda_{pickoff}(R)) + \lambda_{3-\gamma}$$

- probability that Ps is inside a sphere with radius R - R_a

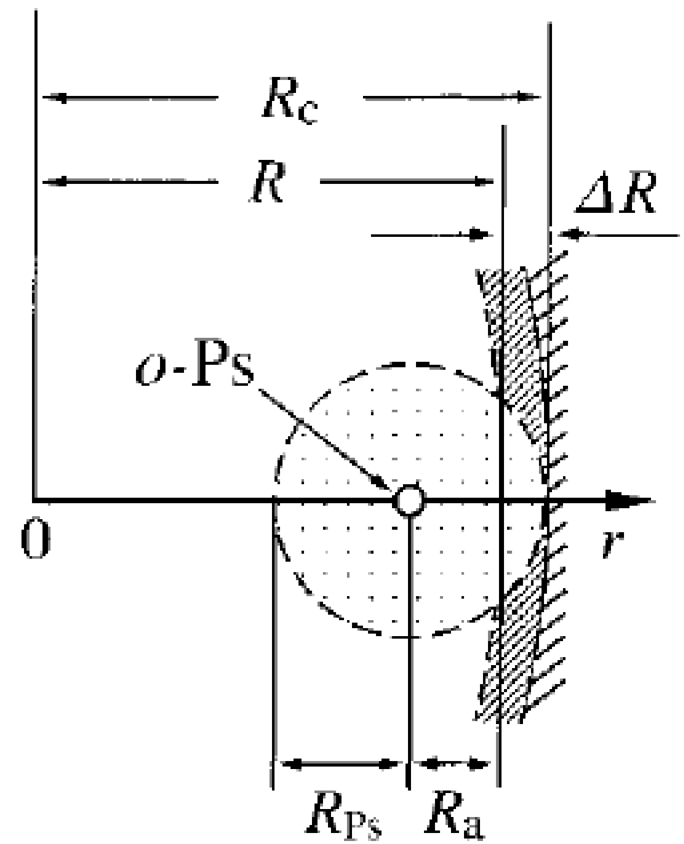
$$f(R) = \frac{3}{4\pi}\frac{1}{(R+\Delta R)^3}\int_0^{2\pi}\int_0^{\pi}\int_0^{R-R_a}\rho(r)r^2\sin\theta\, dr\, d\theta\, d\varphi$$

$$\xi = \frac{r}{R+\Delta R} \qquad 0 \le \xi \le 1$$

$$f(R) = \frac{3}{4\pi}\int_0^{2\pi}\int_0^{\pi}\int_0^{(R-R_a)/(R+\Delta R)}\rho(\xi)\xi^2\sin\theta\, d\xi\, d\theta\, d\varphi$$

$$f(R) = \left(\frac{R-R_a}{R+\Delta R}\right)^b$$

pokud $\rho(\xi) = 1 \Rightarrow b = 3$

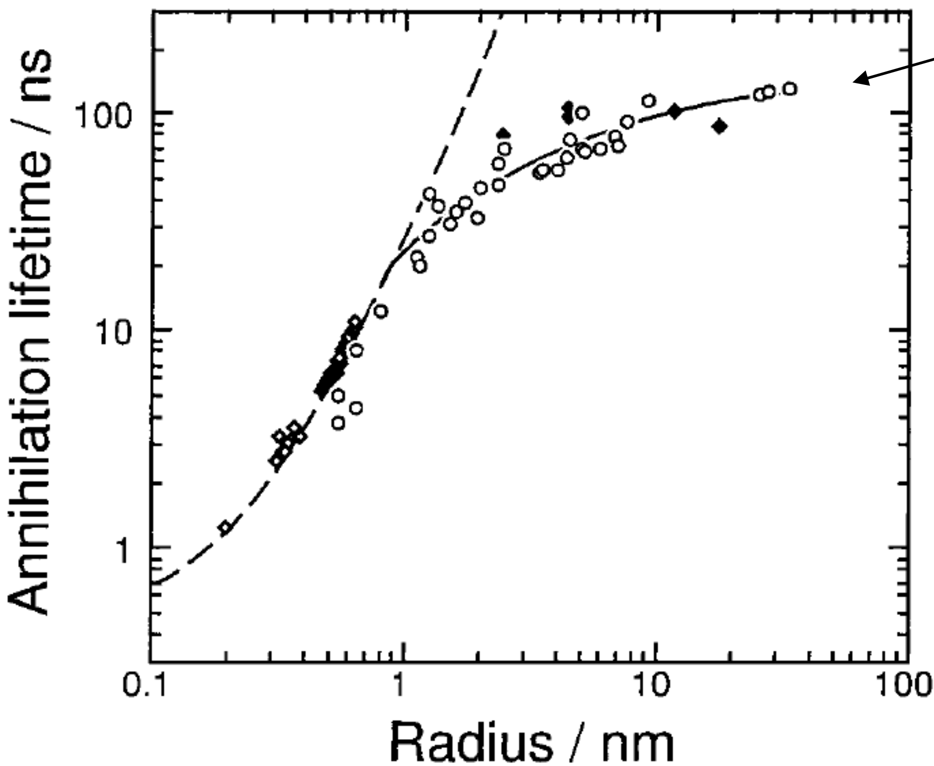


o-Ps pick-off annihilation

- generalization of Tao-Eldrup model for large pores (Ito 1999)
- probability that Ps is inside a sphere with radius R - R_a

$$f(R) = \left(\frac{R - R_a}{R + \Delta R} \right)^b$$

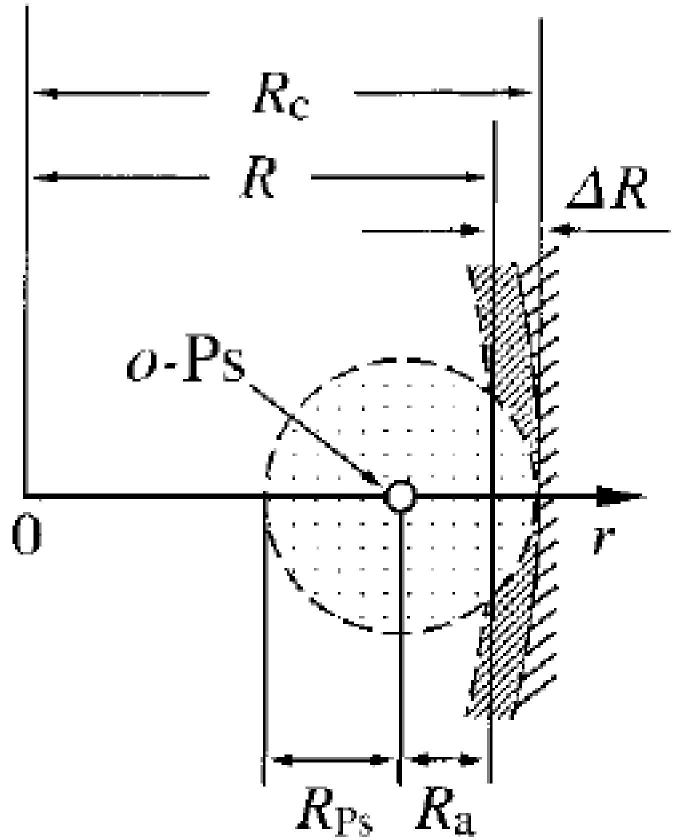
fit b and R_a



from fit:

$b = 0.55$

$R_a = 0.8$ nm

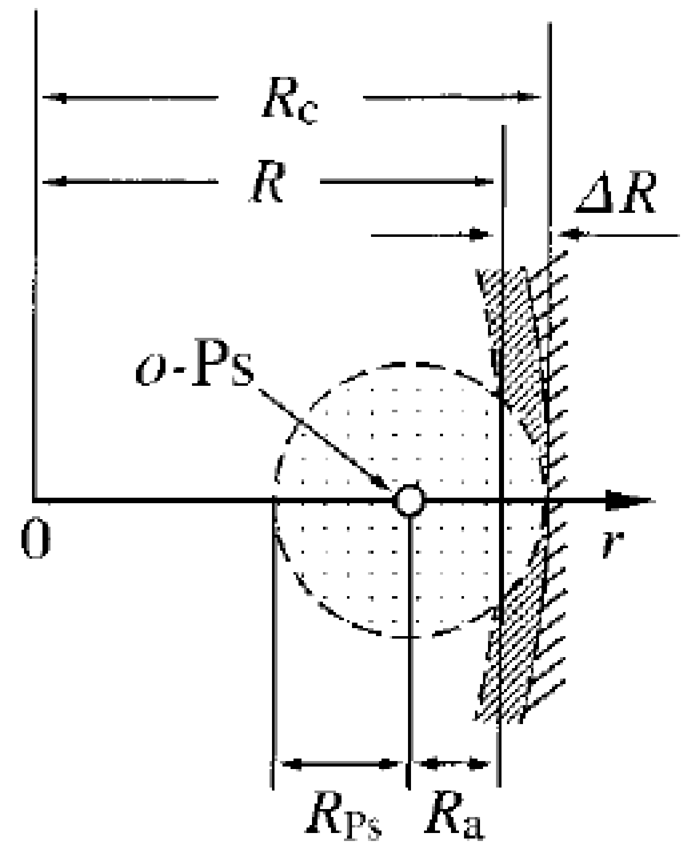


o-Ps pick-off annihilation

- generalization of Tao-Eldrup model for large pores (Ito 1999)

- annihilation rate of o-Ps in a pore with radius R:

$$\lambda_{o-Ps} = \begin{cases} \lambda_{pickoff}(R)\left(1 - \left(\dfrac{R - R_a}{R + \Delta R}\right)^b\right) + \lambda_{3-\gamma} & R \geq R_a \\ \lambda_{pickoff}(R) + \lambda_{3-\gamma} & R < R_a \end{cases}$$



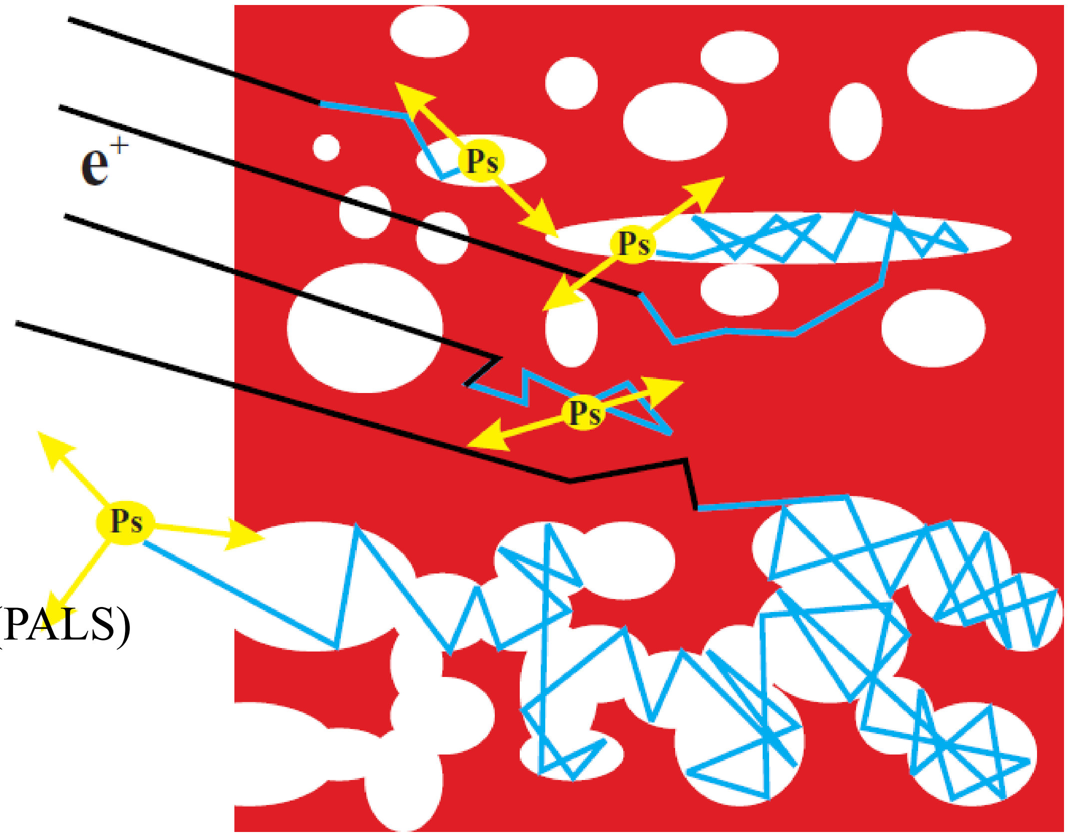
- $R_a = 0.8$ nm

- $b = 0.55$

- $\Delta R = 0.1656$ nm

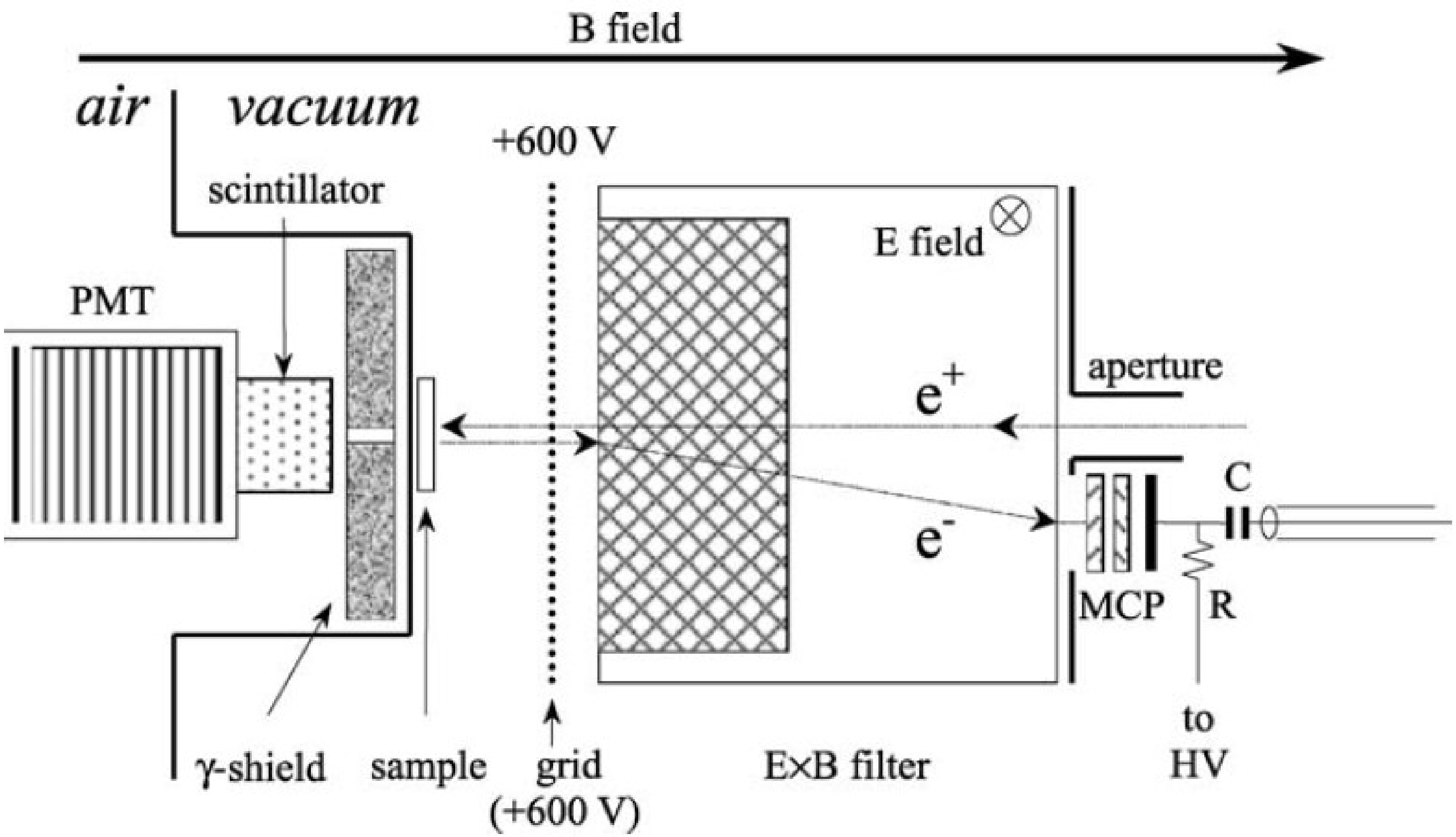
Techniques of Ps probing of porous materials

- Doppler broadening (DB)
- Angular correlation (ACAR)
- Ps time of flight measurement (Ps-TOF)
- positron annihilation lifetime spectroscopy (PALS)



Positron annihilation lifetime spectroscopy (PALS)

• Ps lifetime measurement – slow positron beam

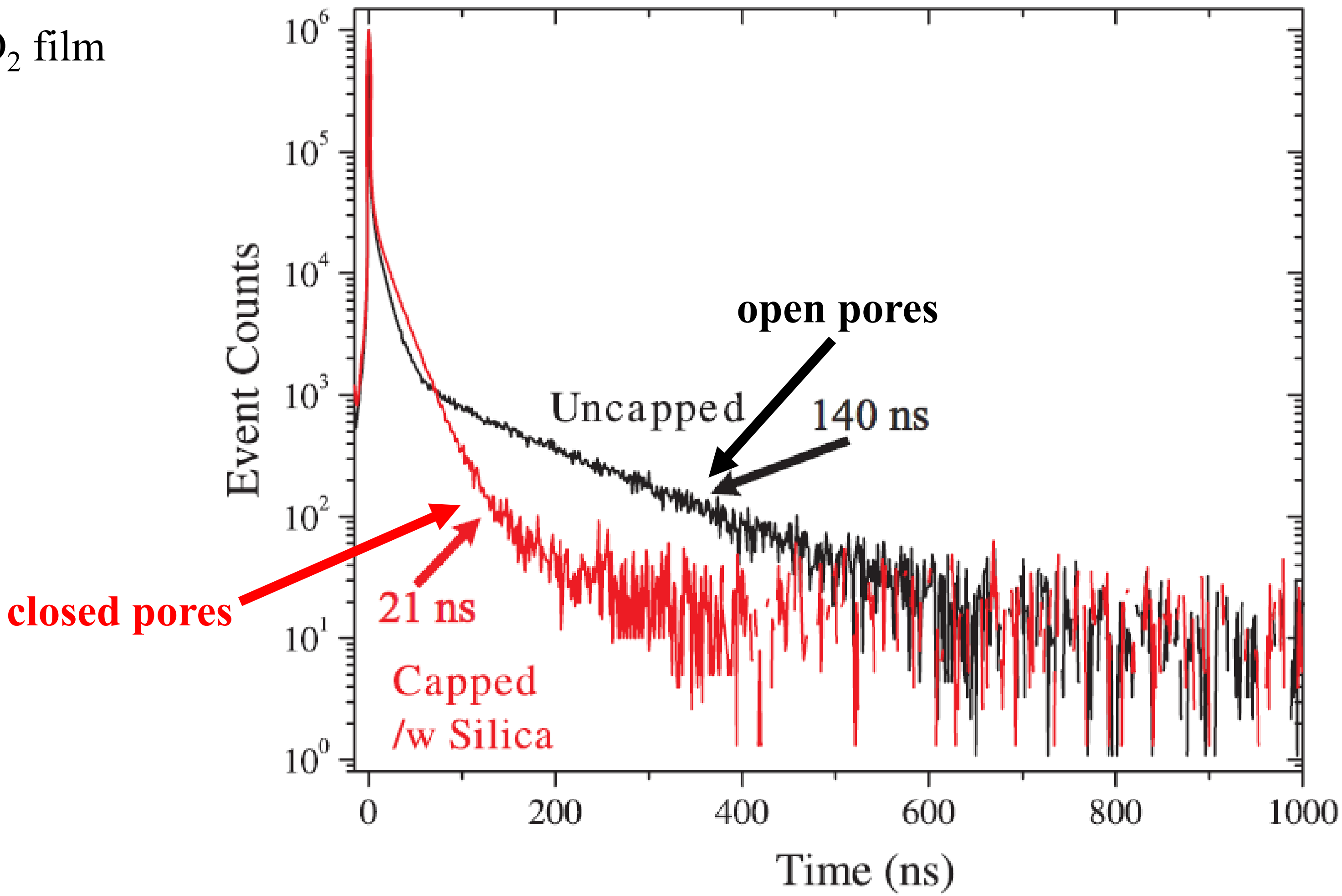


Washington State University, USA

Positron annihilation lifetime spectroscopy (PALS)

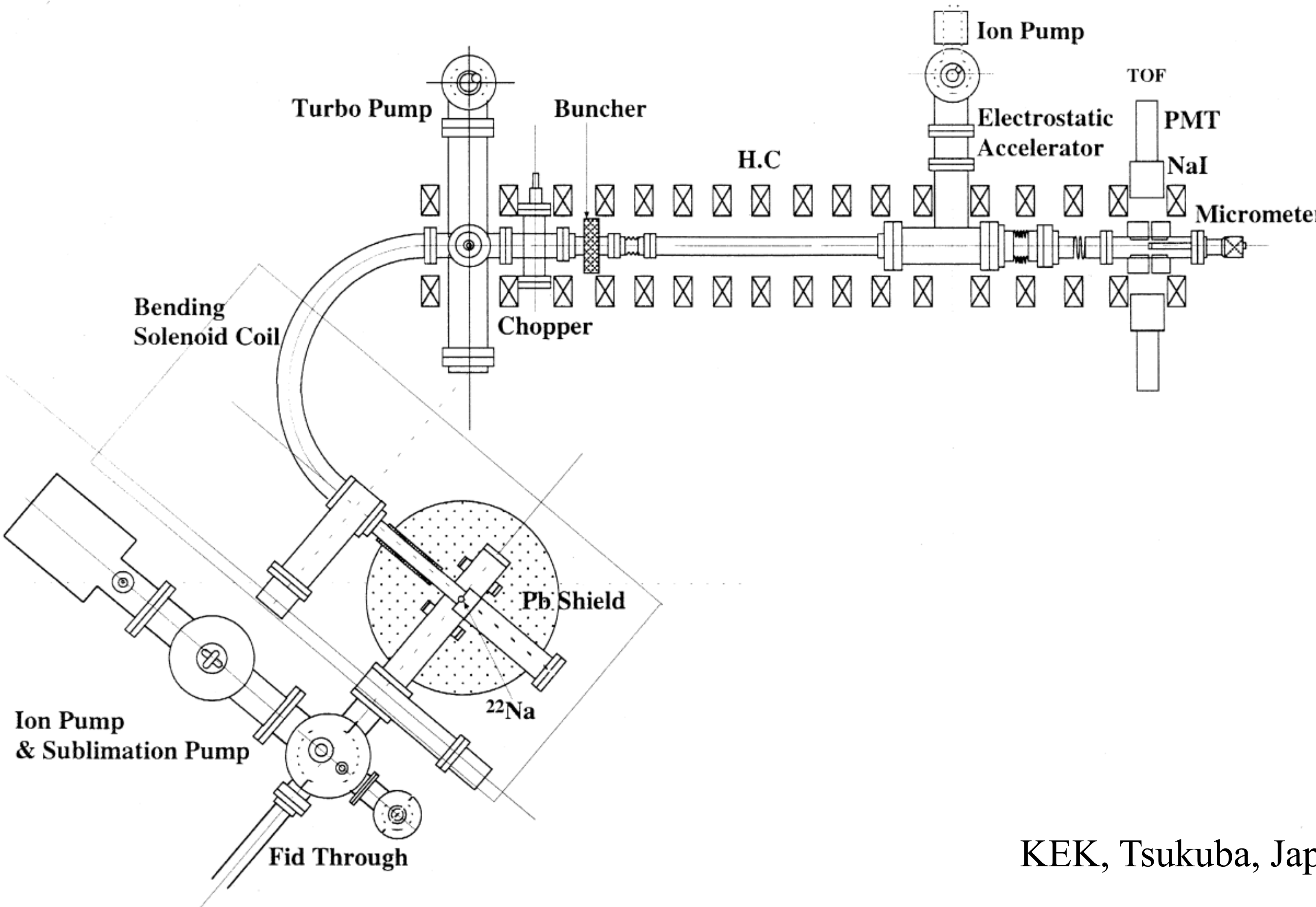
- Ps lifetime measurement – slow positron beam

- SiO_2 film



Ps time of flight measurement (Ps – TOF)

- Ps time of flight measurement: Ps-TOF (Ps time of flight)



KEK, Tsukuba, Japan

Ps time of flight measurement (Ps – TOF)

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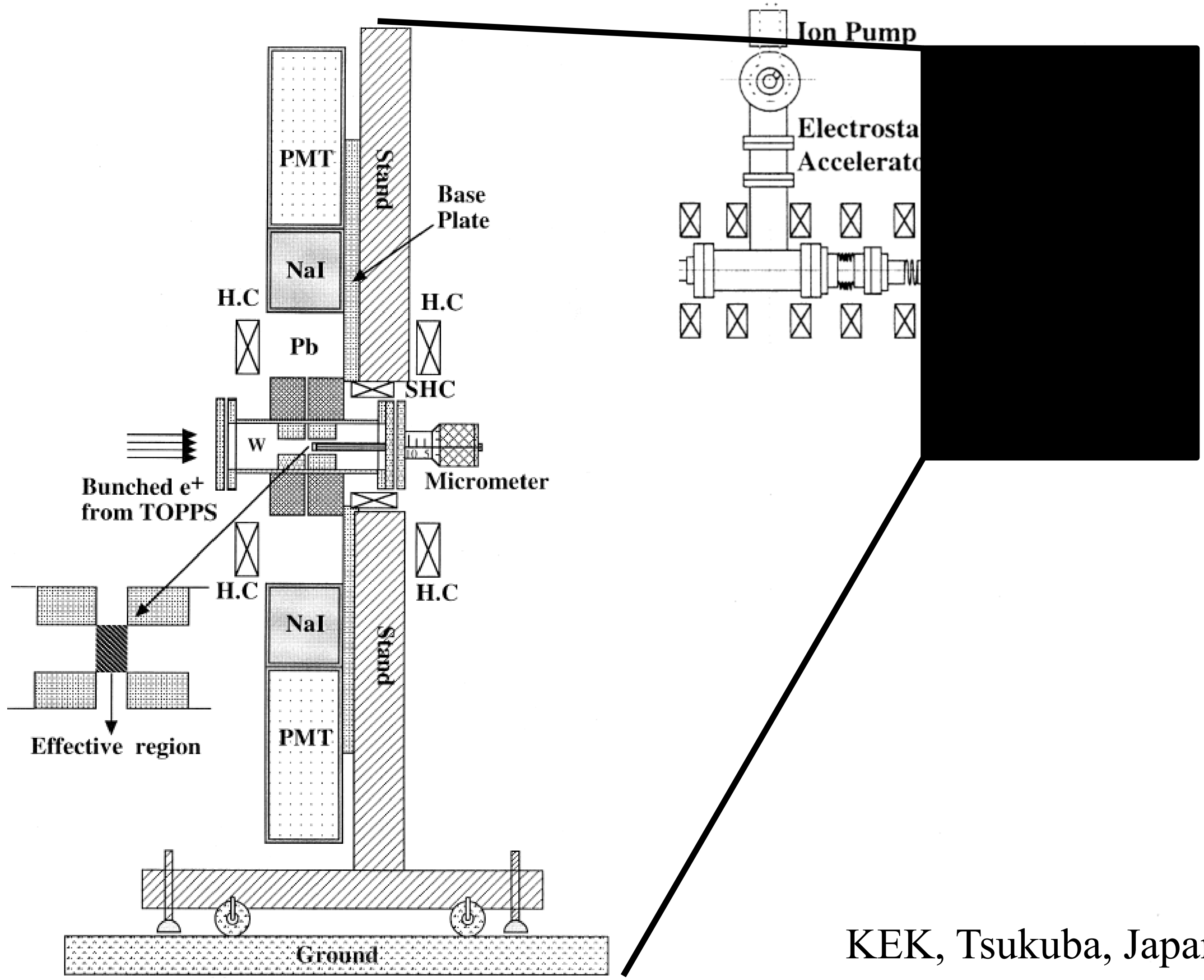

KEK, Tsukuba, Japan

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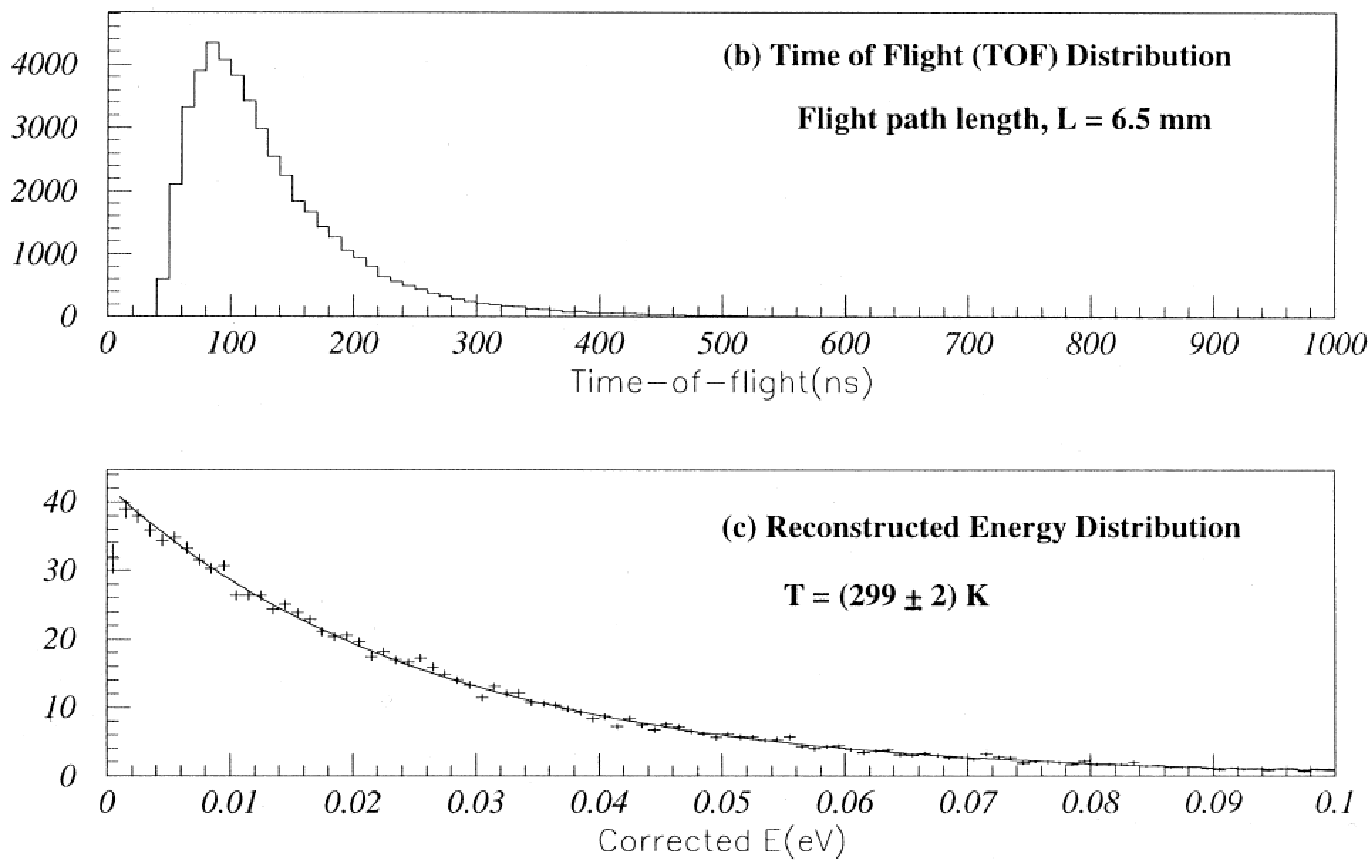


KEK, Tsukuba, Japan

Doppler broadening - DB

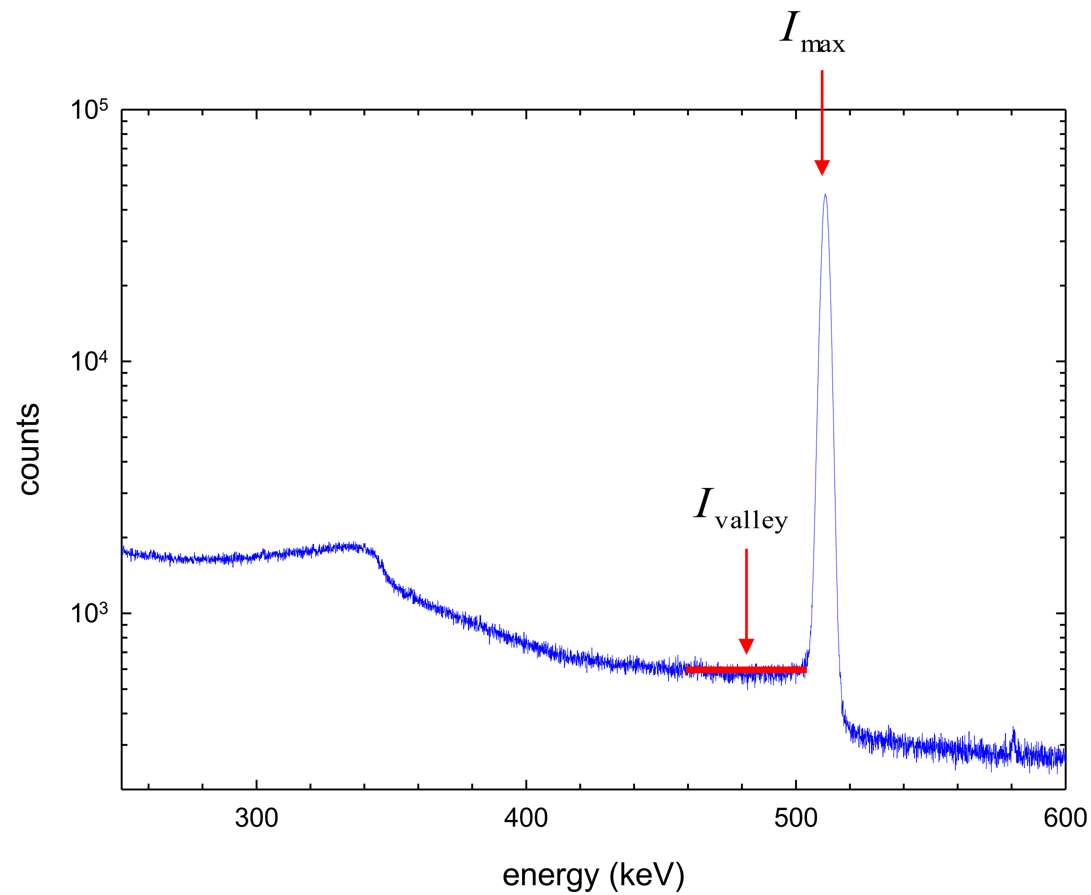
- Doppler broadening spectroscopy (DB)

$$R = \frac{I_{\text{valley}}}{I_{\max}}$$

- F - parameter

$$F = \frac{R - R_0}{R_{\max} - R_0}$$

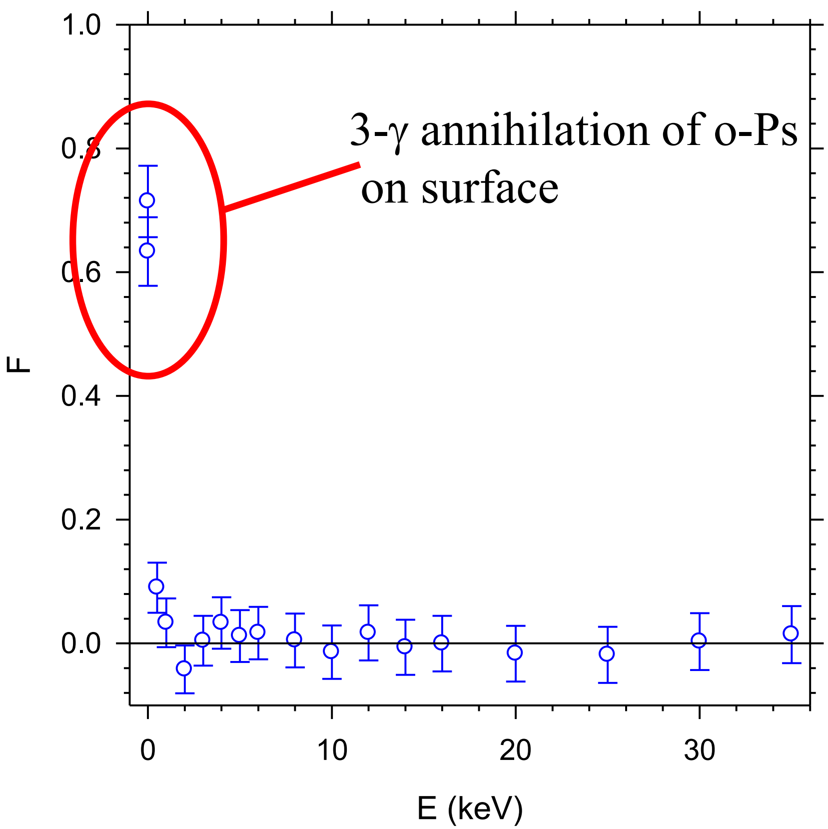
- R_0 – material without Ps
- $R_{\max}$ – material with maximum Ps yield



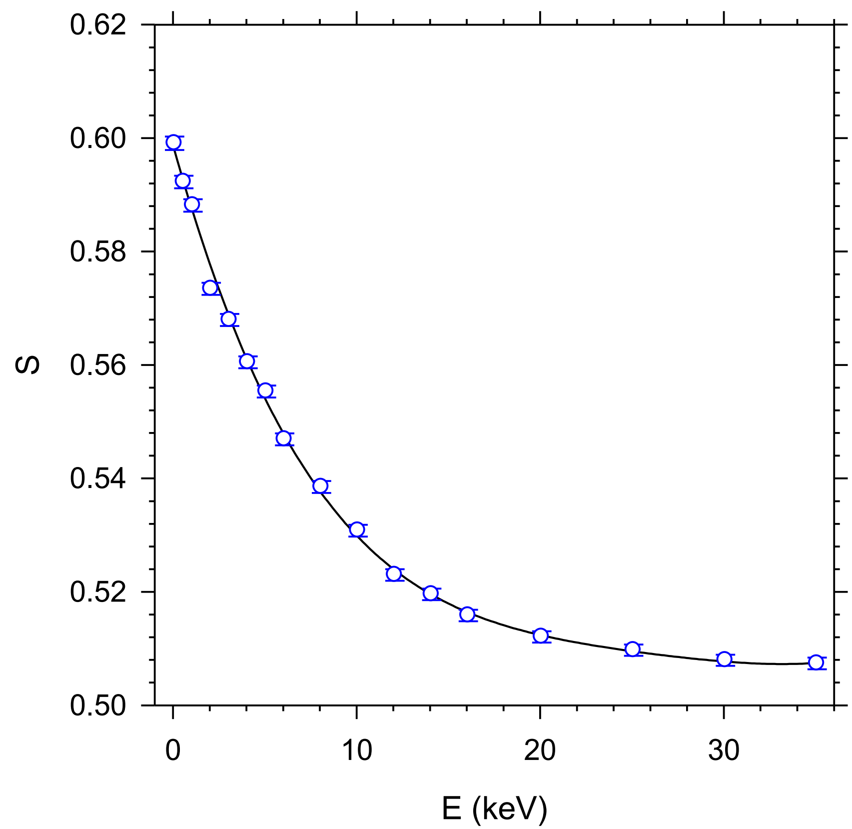
3-γ annihilation of o-Ps

- DB measurement on slow positron beam
- sample: pure Fe

***F* - parameter**



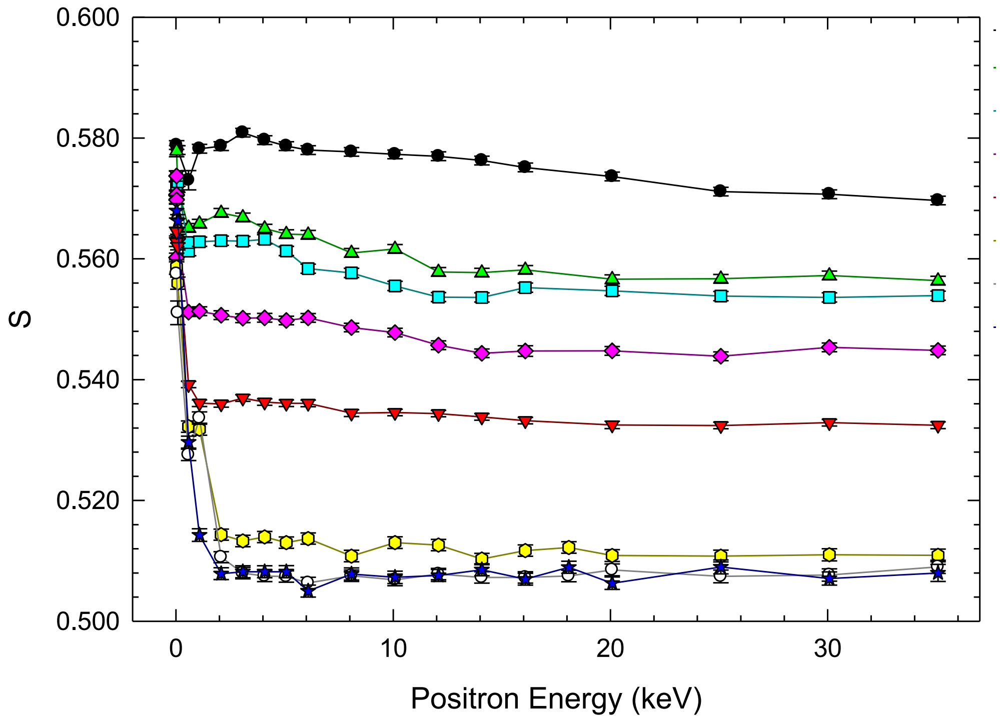
***S* - parameter**



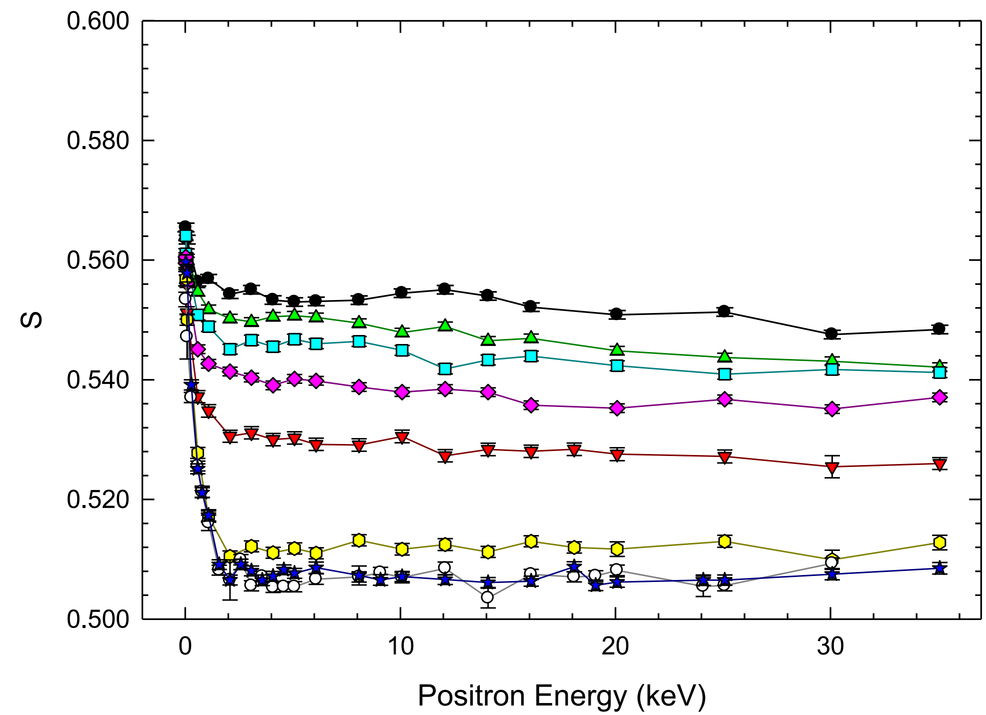
Sintering of ZrO_2 based nanopowders

- DB measurement on slow positron beam
- reduction of porosity during sintering

ZrO_2 + 3 mol.% Y_2O_3



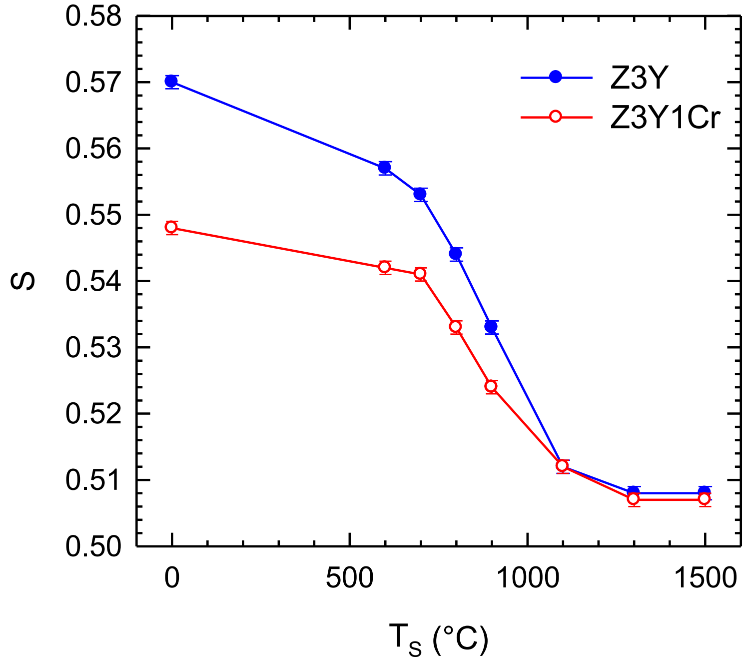
ZrO_2 + 3 mol.% Y_2O_3 + 1 mol. % Cr_2O_3



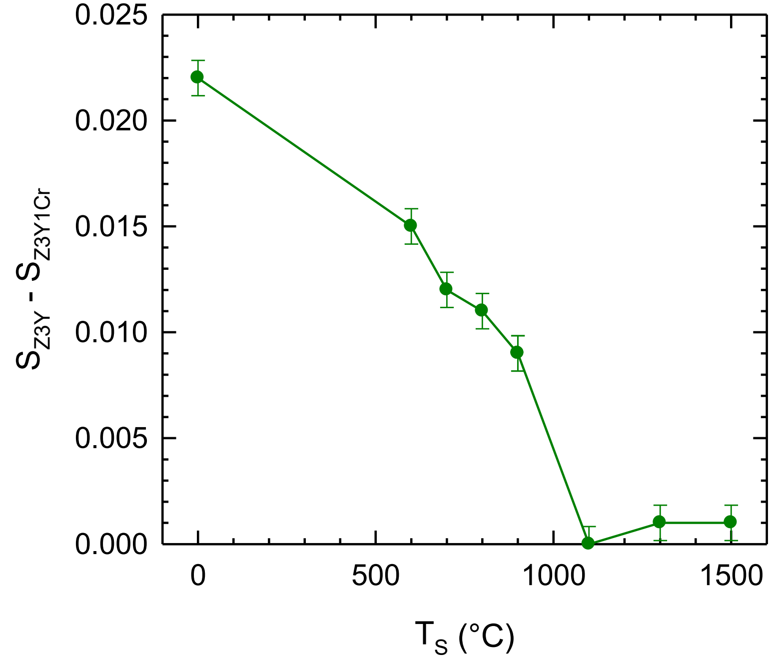
Sintering of ZrO_2 based nanopowders

- **ZrO_2 + 3 mol.% Y_2O_3 (Z3Y)**
- **ZrO_2 + 3 mol.% Y_2O_3 + 1 mol. % Cr_2O_3 (Z3Y1C)**

bulk values of *S*-parameter



difference



Sintering of ZrO_2 based nanopowders

- **ZrO_2 + 3 mol.% Y_2O_3 (Z3Y)**

***F*-parameter**