"Characterization of nanoporous materials by positron annihilation spectroscopy"

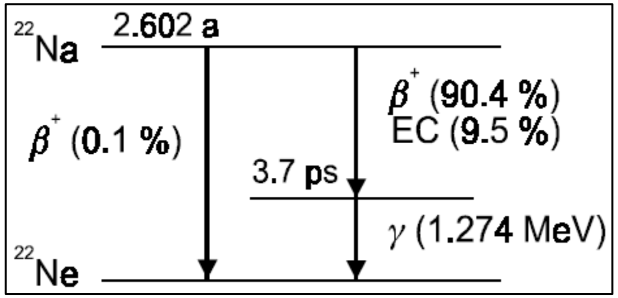
R.Krause-Rehberg
S.Thraenert, E.M.Hassan, D.Enke

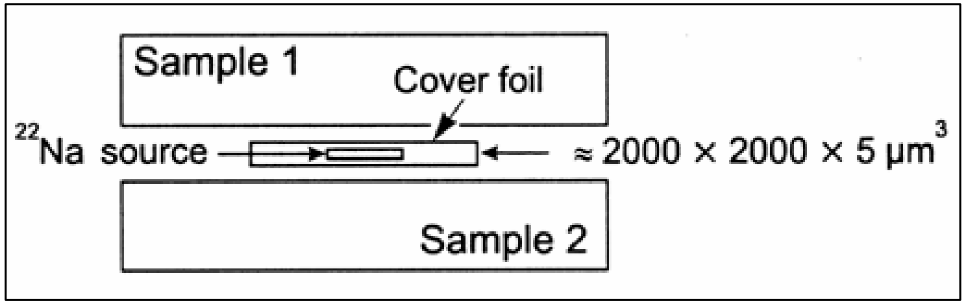
Martin-Luther-Universität
Halle-Wittenberg

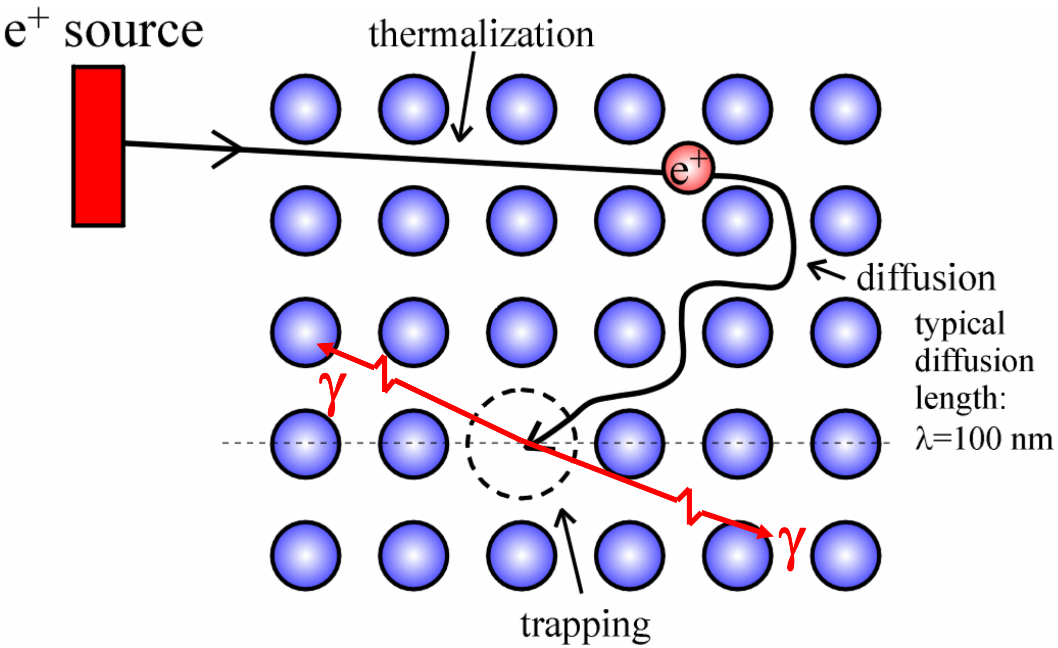
Characterization of nanoporous materials by positron annihilation spectroscopy

- Positron annihilation lifetime spectroscopy (PALS)
- Application in crystalline materials
- Positronium as bound state of Positron and Electron
- Characterization of nanopores by Positronium lifetime spectroscopy

Basics of Lifetime Spectroscopy





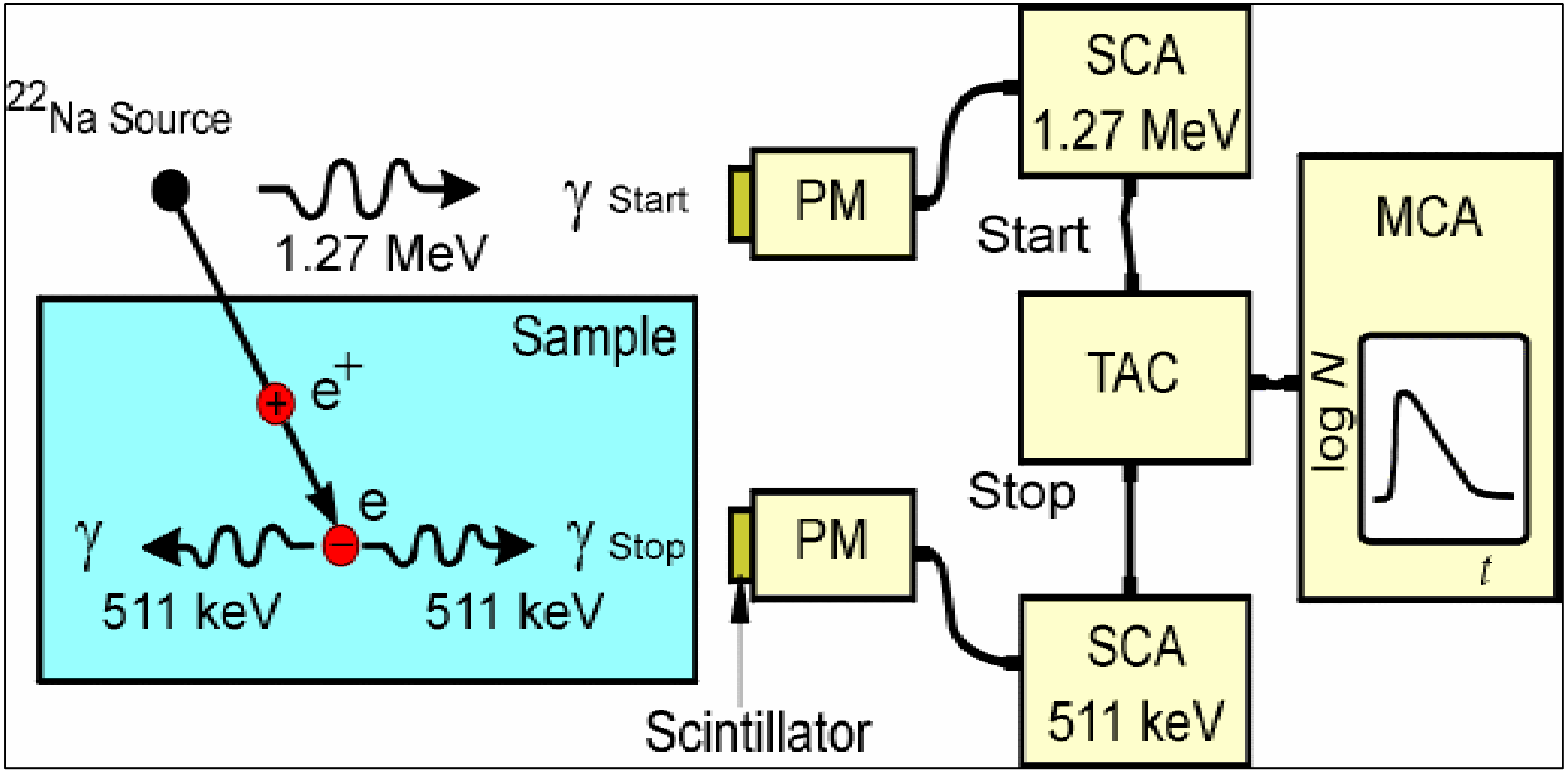


Positrons

- **thermalize (reach thermal energies)**
- **diffuse**
- **being trapped**
- **and annihilate**

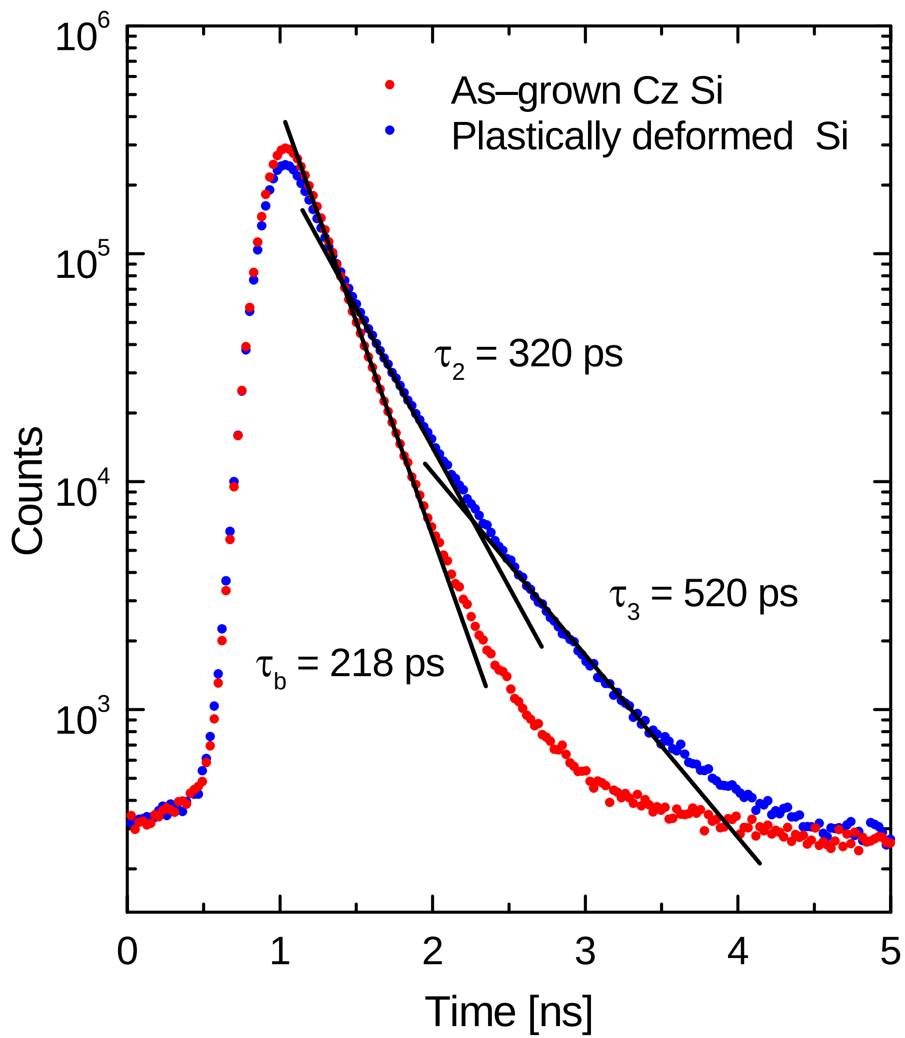
When positron trapped in vacancies: Lifetime increases due to smaller electron density in open volume

Lifetime Measurement



Positron lifetime: time between 1,27 MeV and 0,511 MeV quanta

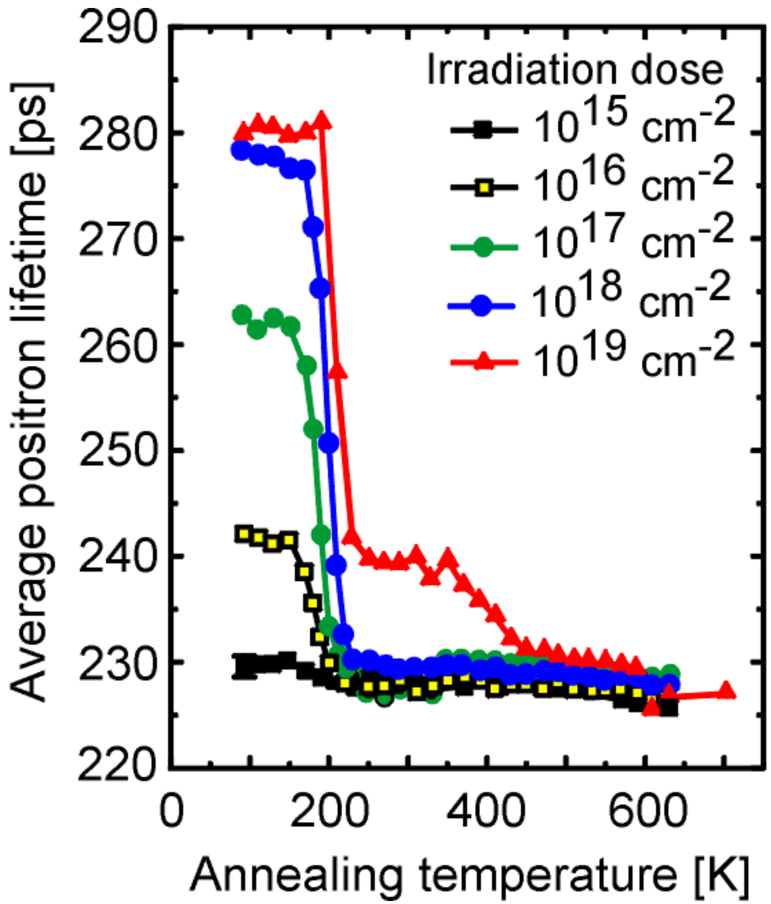
Lifetime Spectrum



- lifetime spectra consist of exponential decay components
- positron trapping in open-volume defects leads to long-lived lifetime components
- spectra analysis is performed by non-linear fitting routines after source and background subtraction
- experimental result: lifetimes τ_i and intensities I_i

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

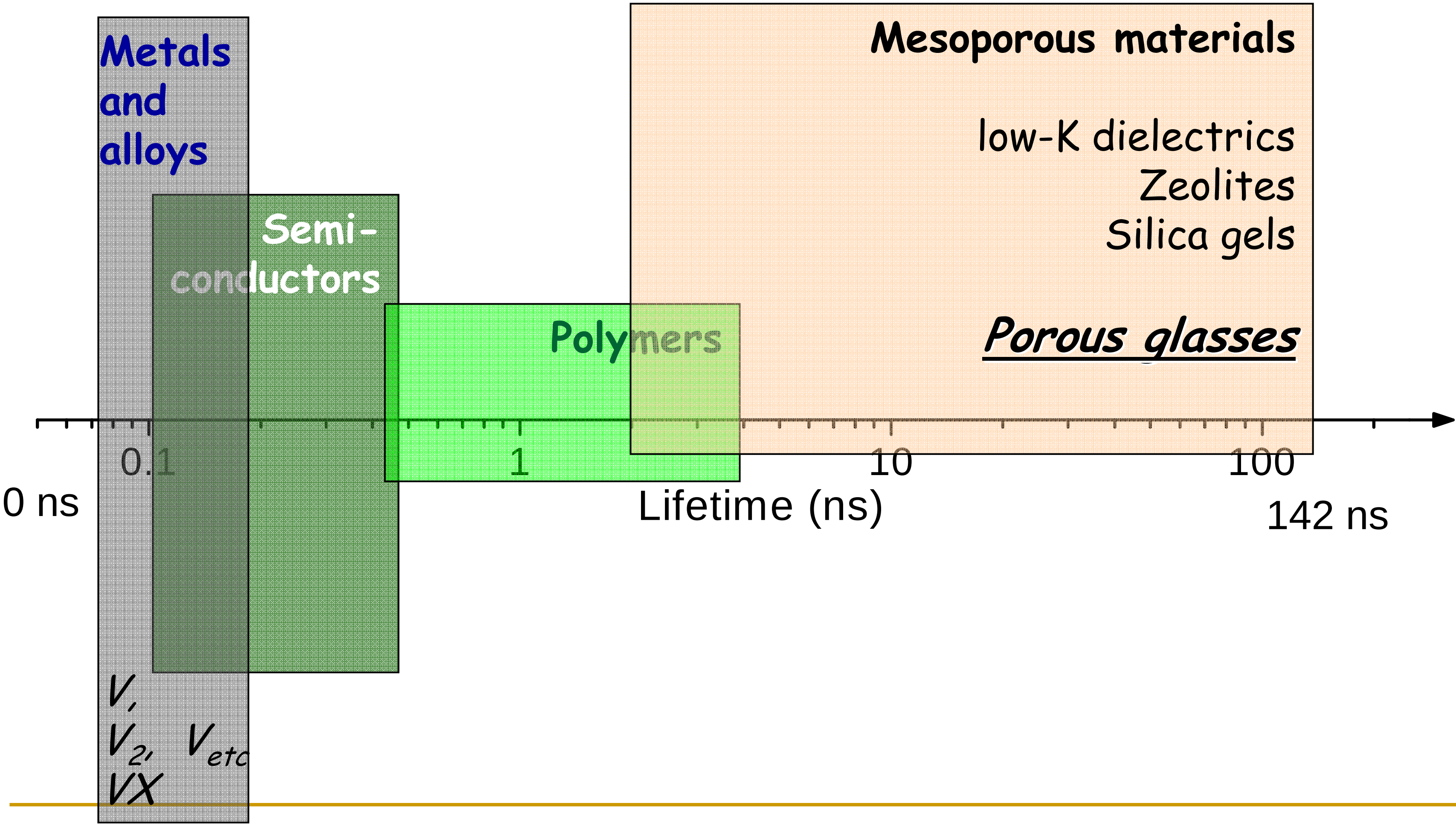
Defects in electron irradiated Ge



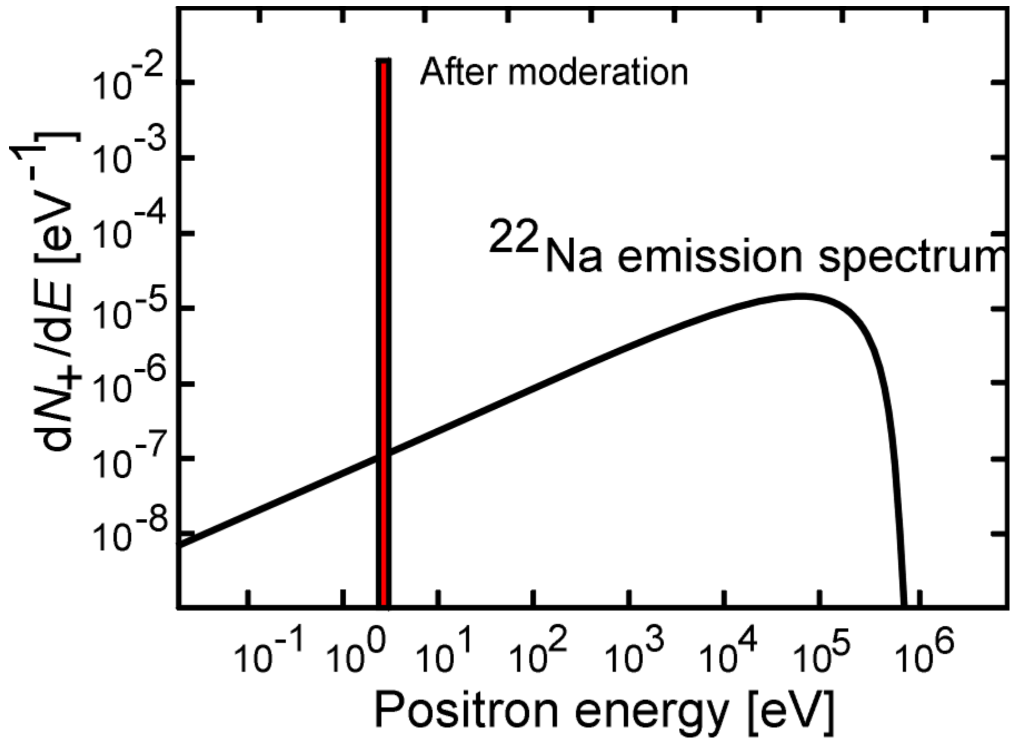
- electron irradiation (2 MeV) at 4K generates Frenkel pairs
- vacancy annealing and defect reactions may be studied

(Polity et al., 1997)

Typical lifetimes



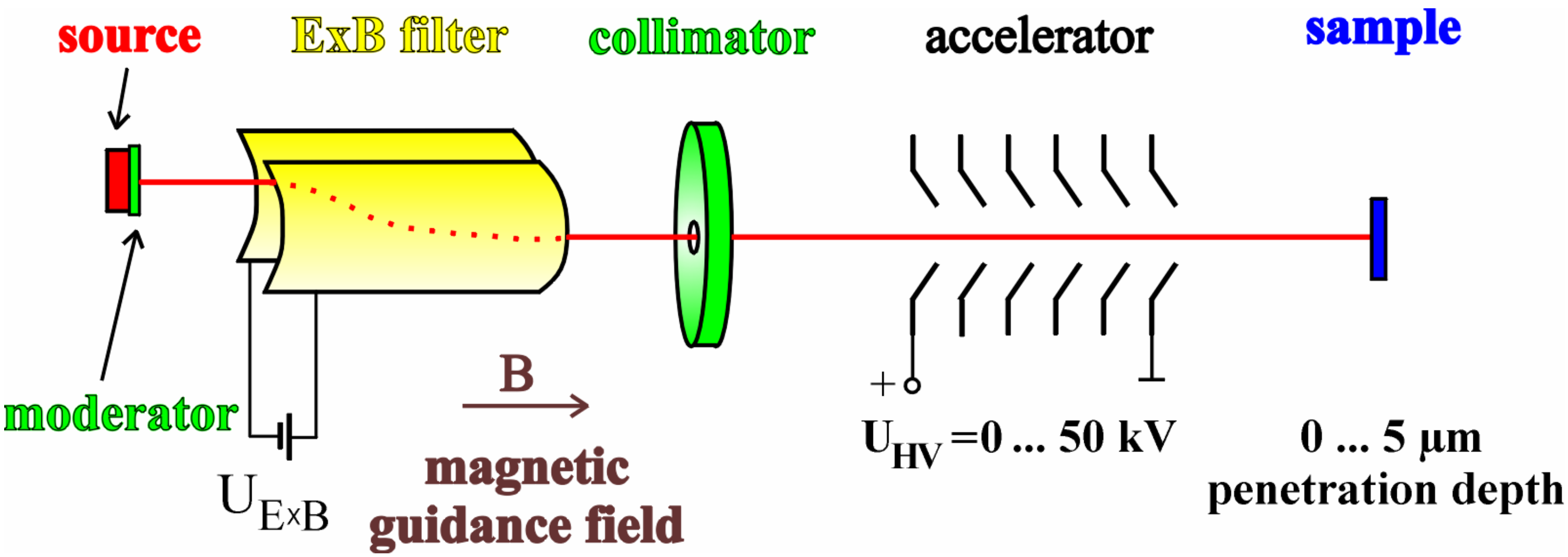
Thermalization



- broad positron emission spectrum
- deep implantation into solids
- not useful for thin layers
- moderation necessary

Mean implantation depth of unmoderated positrons (1/e) in Si: 50μm

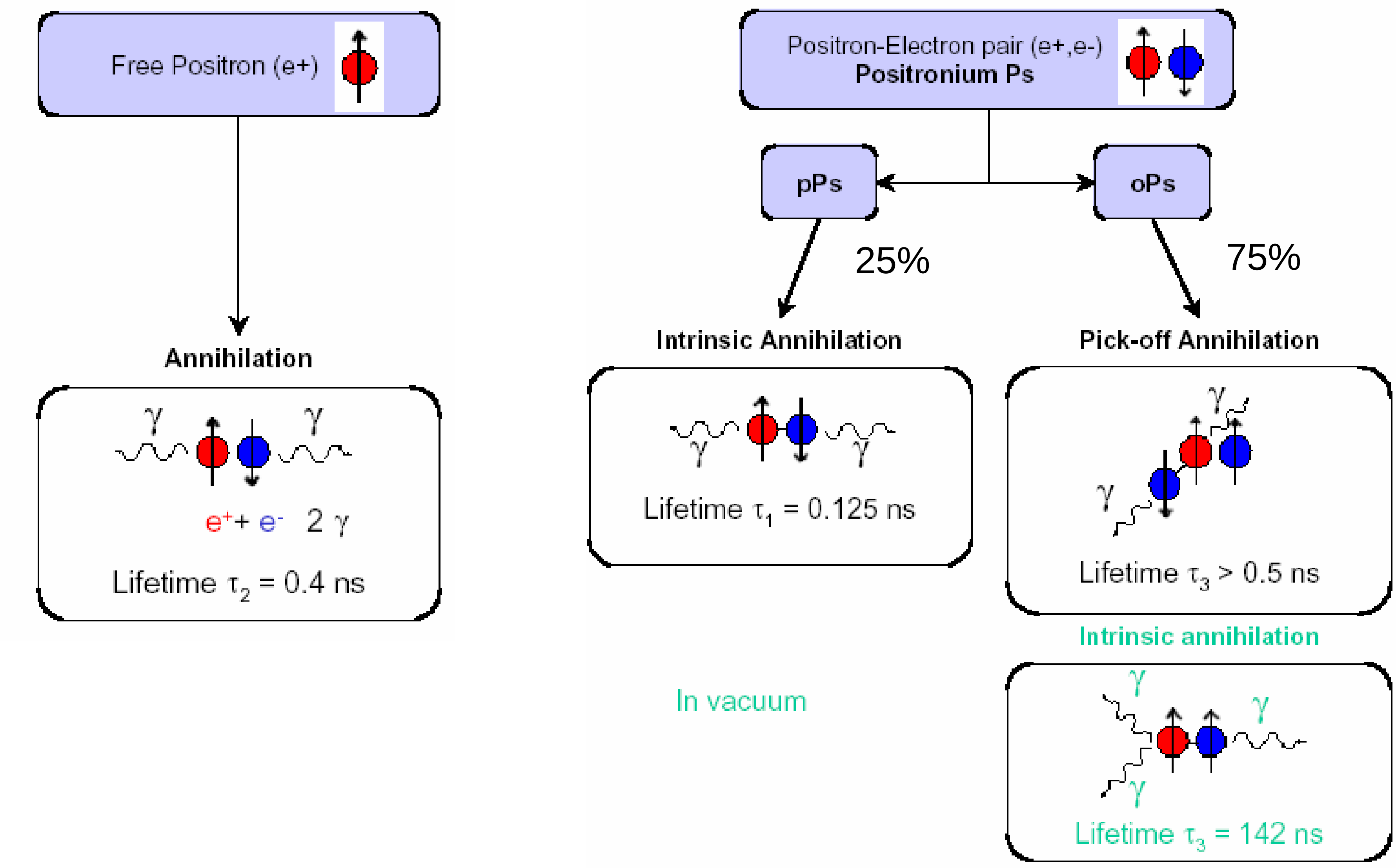
Slow positron beam at Halle



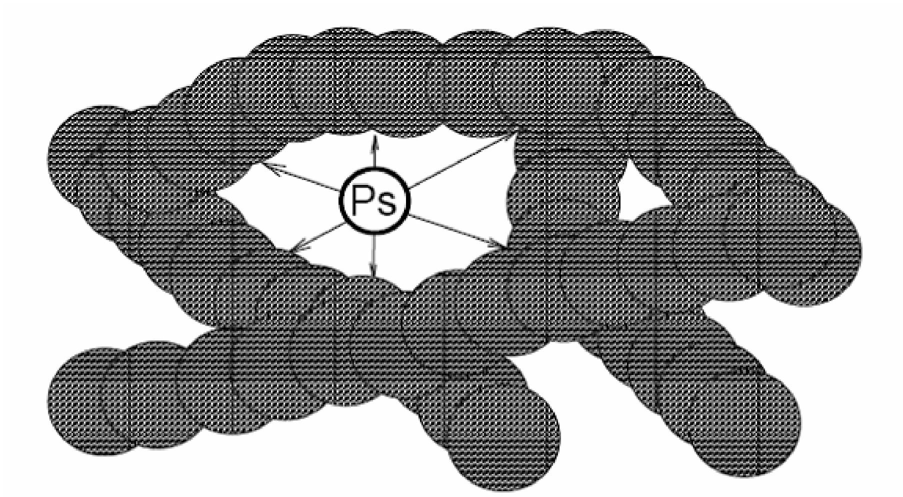
- spot diameter: 5 mm
- time per single spectrum: 20 min
- time per defect-depth scan: 12 hours

Positrons & Positronium

In materials without free electrons Positronium may be formed (Polymers, glass, liquids, gases).



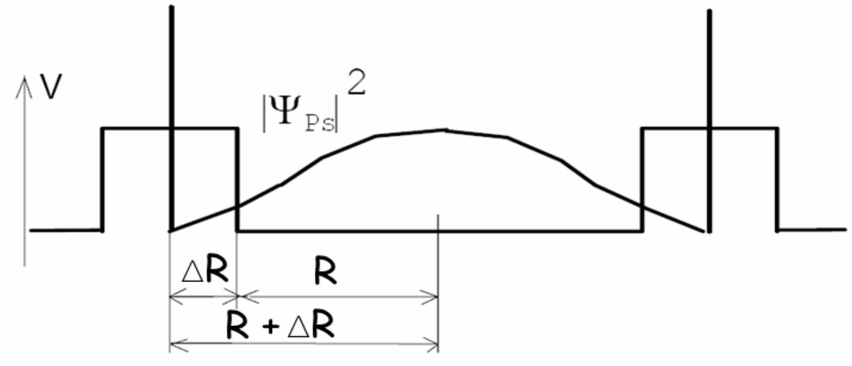
Pick-off Annihilation of o-Ps



pick-off annihilation

- o-Ps is converted to p-Ps by capturing an electron with anti-parallel spin
- happens during collisions at walls of pore
- lifetime decreases rapidly
- lifetime is function of pore size 1 ns ... 142 ns

The TE model



- **Annihilation rate:** $\frac{1}{\tau_{o-Ps}} = \lambda_{o-Ps}$

$$= \lambda_{2\gamma} + \lambda_{3\gamma}$$

$$= \lambda_{2\gamma}^0 (P) + \lambda_{3\gamma}^0 (1-P) \cong \lambda_{2\gamma}^0 (P)$$

$$\lambda_{2\gamma}^0 = \frac{\lambda_S + 3\lambda_T}{4} = \lambda_A \approx 2ns^{-1}$$

- **Pore size < 1 nm -> $\lambda_{3\gamma}$ neglected, only pick off annihilation**

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

- ΔR **= 0.166 nm determined by Eldrup**
- **Pore size > 1 nm -> $\lambda_{3\gamma}$ can not be neglected, temperature dependence of o-Ps lifetime (excited states)**

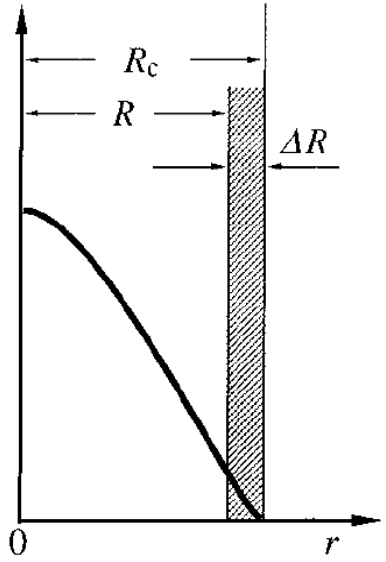
Tao, S. J. *J. Chem. Phys.* **1972**, *56*, 5499-5510. / Eldrup, M.; Lightbody, D.; Sherwood, J. N. *Chem. Phys.* **1981**, *63*, 51-58.

The 2 models for R > 1 nm - Tokyo

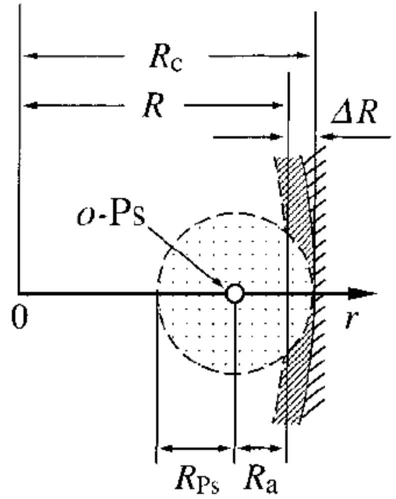
- **Tokyo model:**

$$\lambda_{Tokyo}(R) = \begin{cases} \lambda_{TE} + \lambda_{3\gamma} & (R < R_a) \\ \lambda_{TE}(R_a)\left[1 - \left(\dfrac{R - R_a}{R + \Delta R}\right)^b\right] + \lambda_{3\gamma} & (R \geq R_a) \end{cases}$$

  - **Problems:** - no explicit temperature dependence
    - two free parameters to be determined



(a) TE



(b) Tokyo

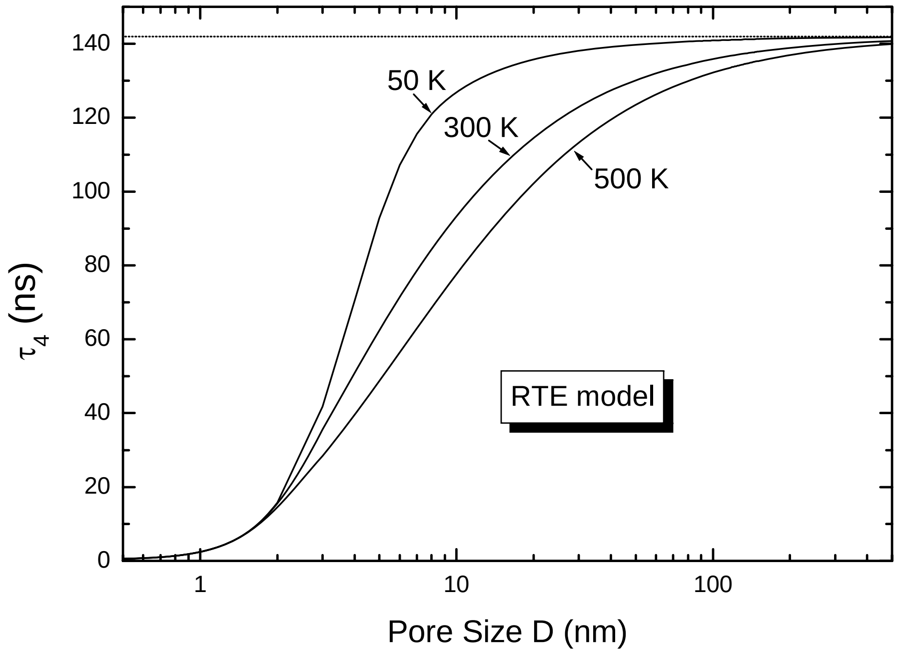
empirical:
R_a = 0.8 nm
b = 0.55

K. Ito, H. Nakanishi, Y. Ujihira, *J. Phys Chem. B* **1999**, *103,* 4555.

The 2 models for R > 1 nm - RTE

- **RTE model (for 3D cubic pores):**

$$\lambda_{RTE}(D,T) = \lambda_A - \frac{\lambda_S - \lambda_{3\gamma}}{4}\left[1 - \frac{2\delta}{D} + \frac{\sum_{i=1}^{\infty} \frac{1}{i\pi}\sin\left(\frac{2i\pi\delta}{D}\right) e^{\left(\frac{-\beta i^2}{D^2 kT}\right)}}{\sum_{i=1}^{\infty} e^{\left(\frac{-\beta i^2}{D^2 kT}\right)}}\right]^3$$

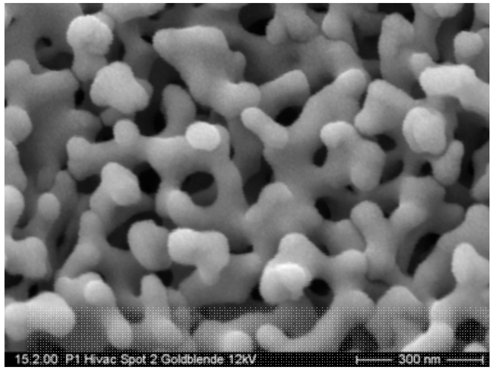


- **Boltzmann statistics ascribes explicit temperature dependence to the lifetime**
- **Rectangular geometry -> prevention of complicated Bessel functions**
- δ **= 0.18 nm analogous to TE model**

D. W. Gidley, T. L. Dull, W. E. Frieze, J. N. Sun, A. F. Yee, *J. Phys. Chem. B* **2001**, *105,* 4657.

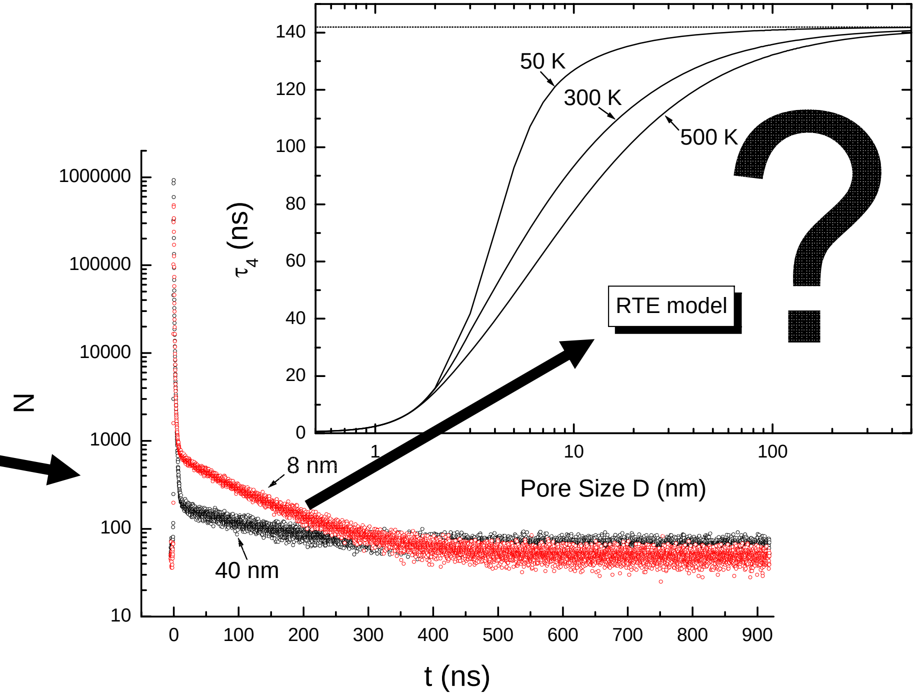
Verifying the RTE model

- Porous Vycor Glass

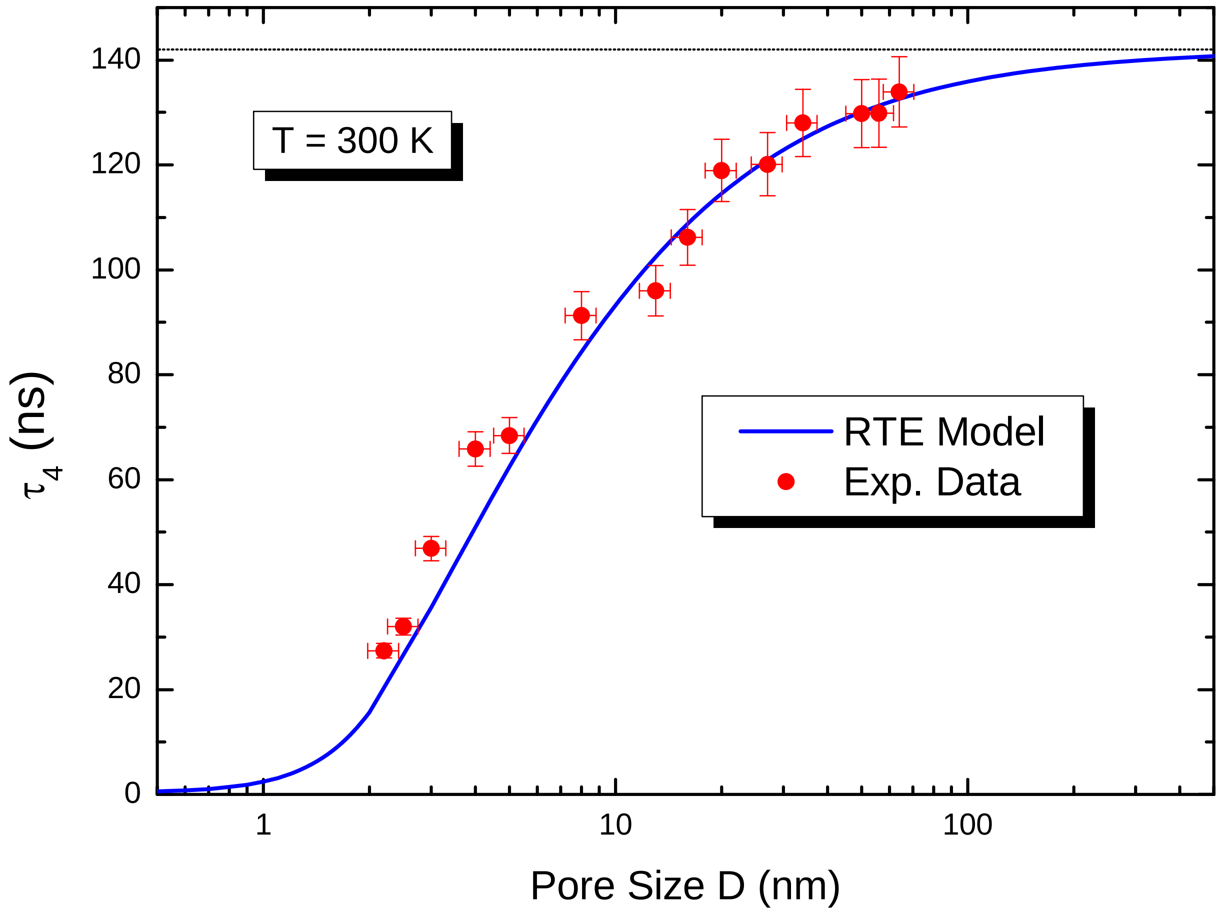


- RTE-Model: the state of the art

- Experimental results



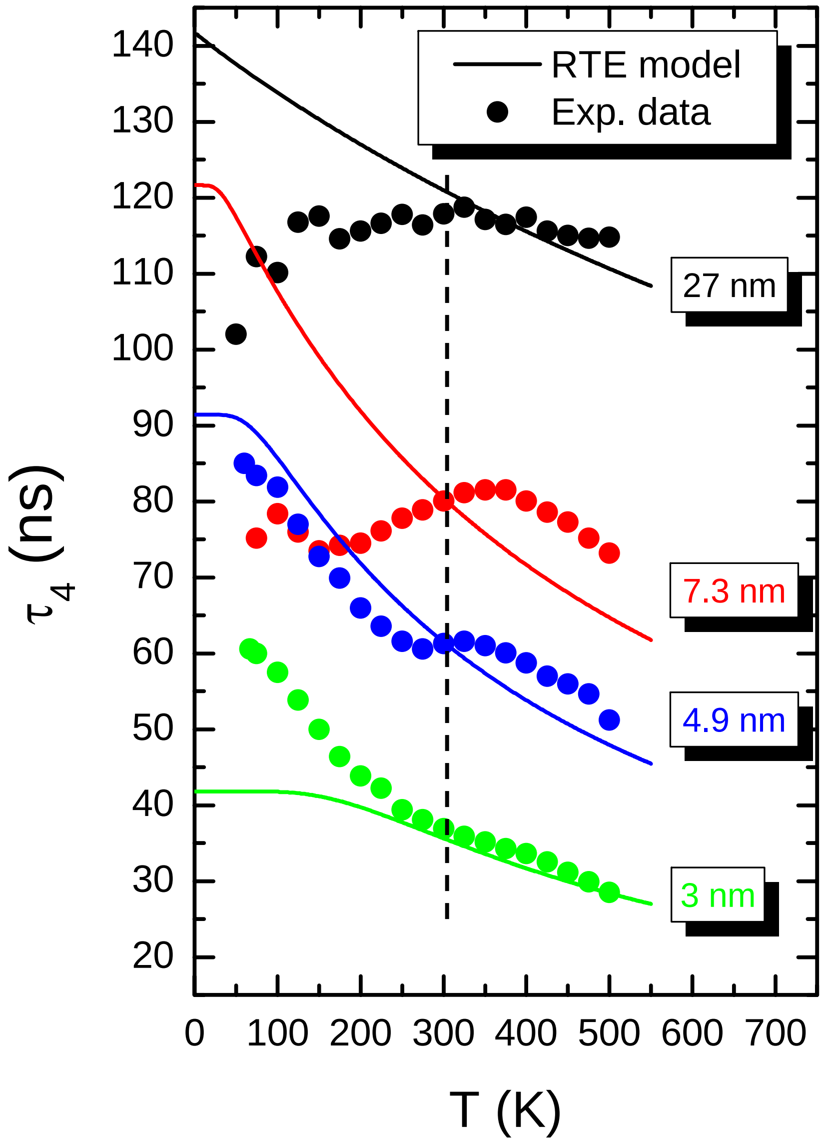
The experiments at T = 300 K



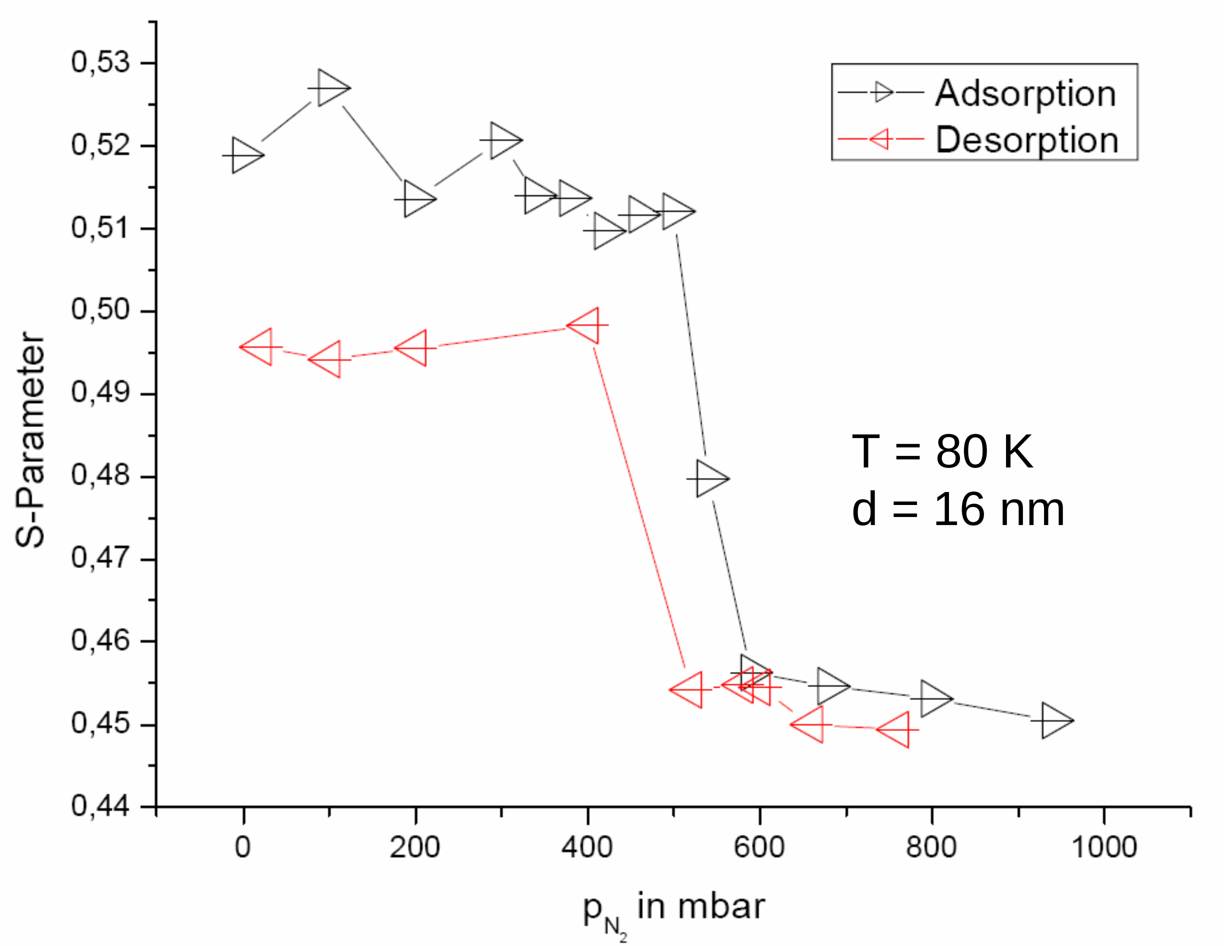
- we measured porous glass in a broad pore size range
- pore size obtained by N_2-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size

Temperature Dependence

- although we found good agreement for T = 300 K
- temperature behavior cannot be explained very well at low temperatures
- model too simple



Observation of cryo-condensation in nano-pores



- S-parameter behaves similar like intensity of o-Ps lifetime component
- cryo-condensation can be observed as filling of pores
- phase transition can be studied in a nano-volume as function of size, gas, T and p

Summary

- Time spectroscopy of o-Ps is a very sensitive tool for characterization of nano-pores
- most sensitive in range 0.5 … 30 nm
- closed and open pores
- positron beam can be used: fully non-destructive (no contact to sample)