Characterisation of mesopores - ortho-Positronium lifetime measurement as a porosimetry technique

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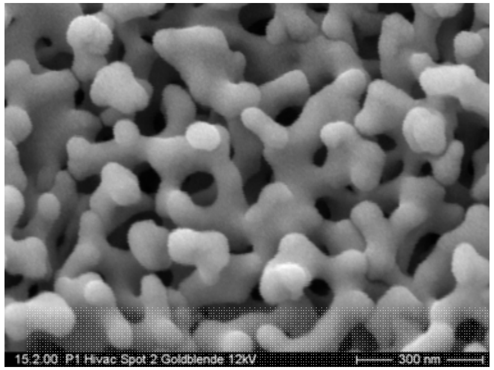
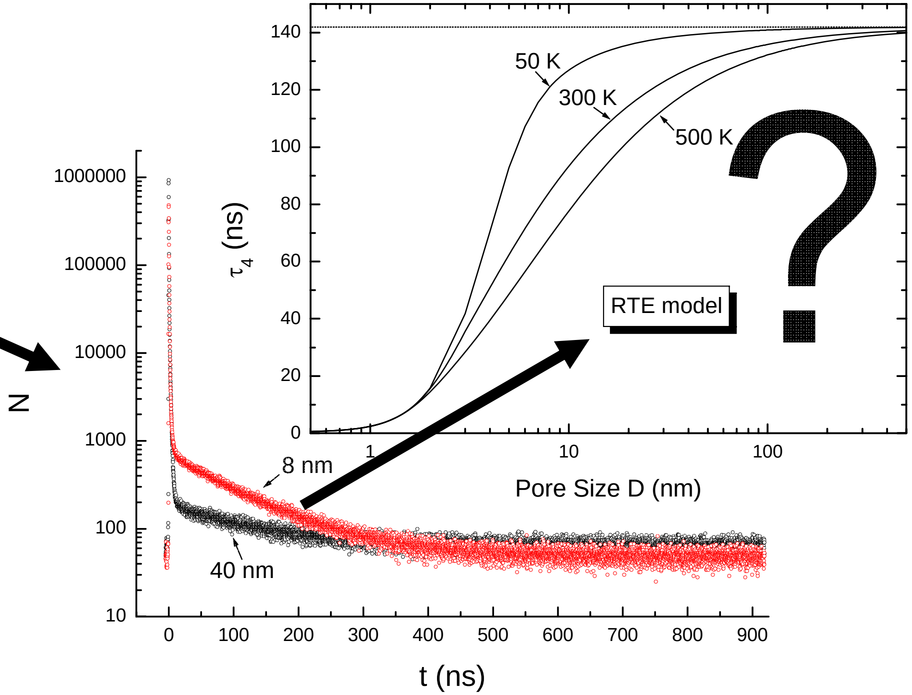
Dresden

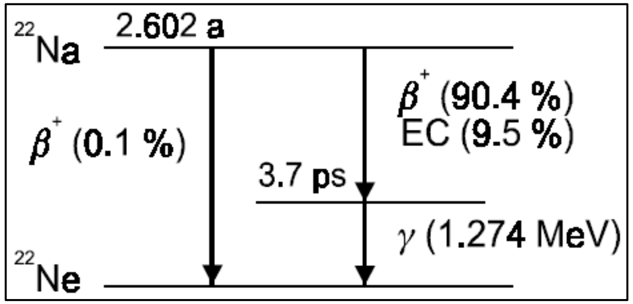
Characterising mesopores

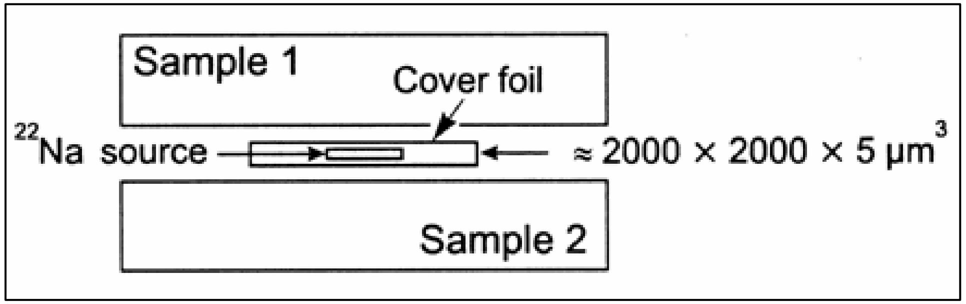
- **Principles of PALS**
  - Lifetime Measurement
  - Positronium
- **Porous glass - CPG**
  - Synthesis
  - Properties
- **Models – the state of the art**
  - Tao Eldrup
  - Tokyo
  - RTE
- **Experimental results**
  - Relation to RTE
- **Summary**

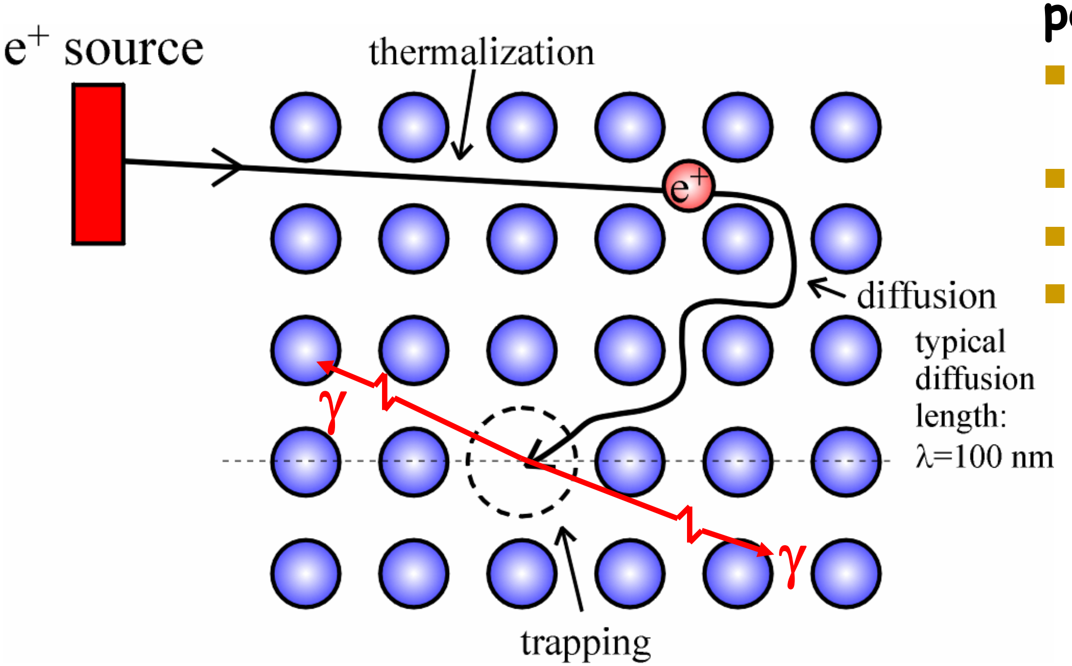




Principles of PALS







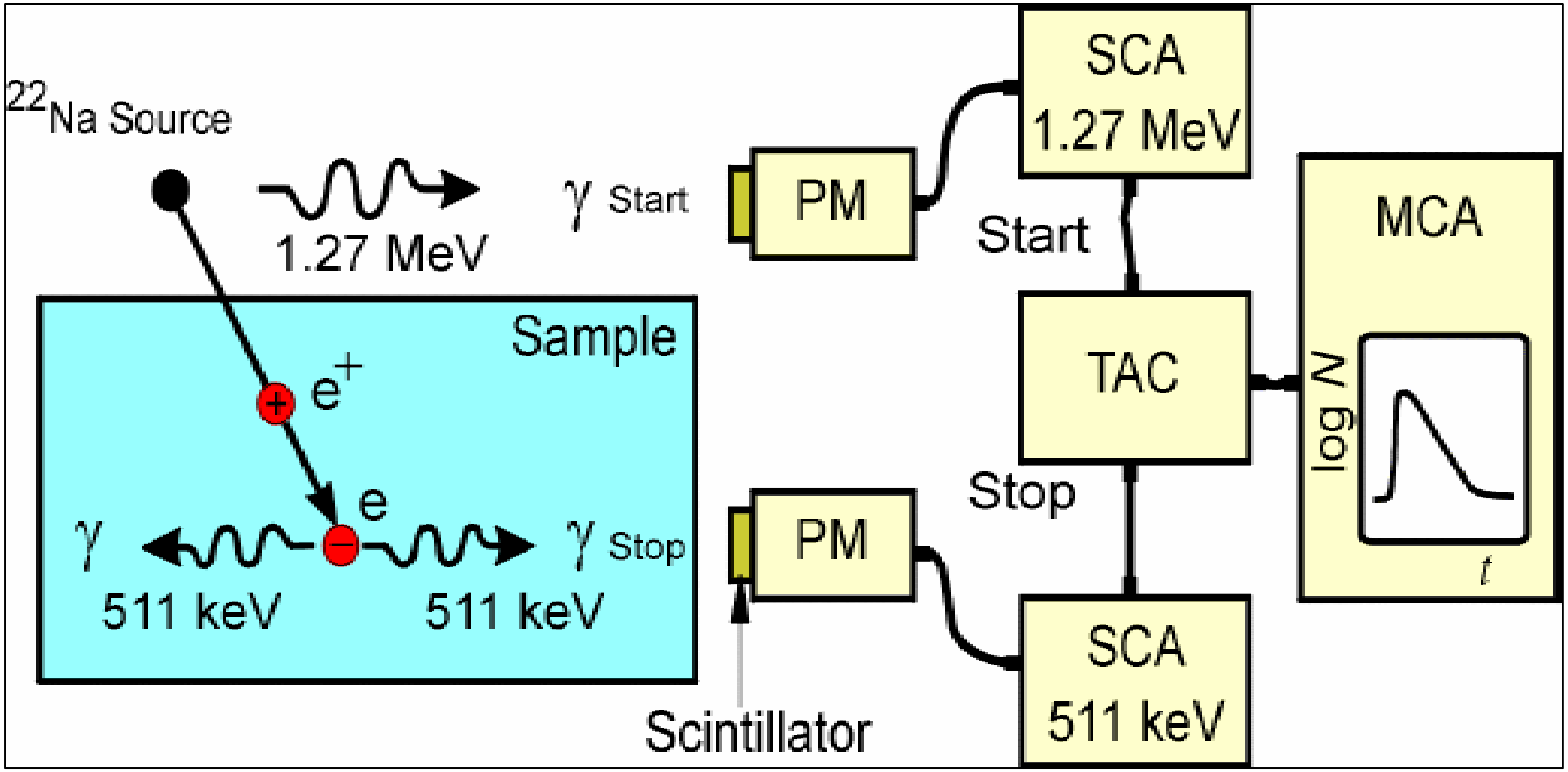
positrons:

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

When trapped in vacancies:

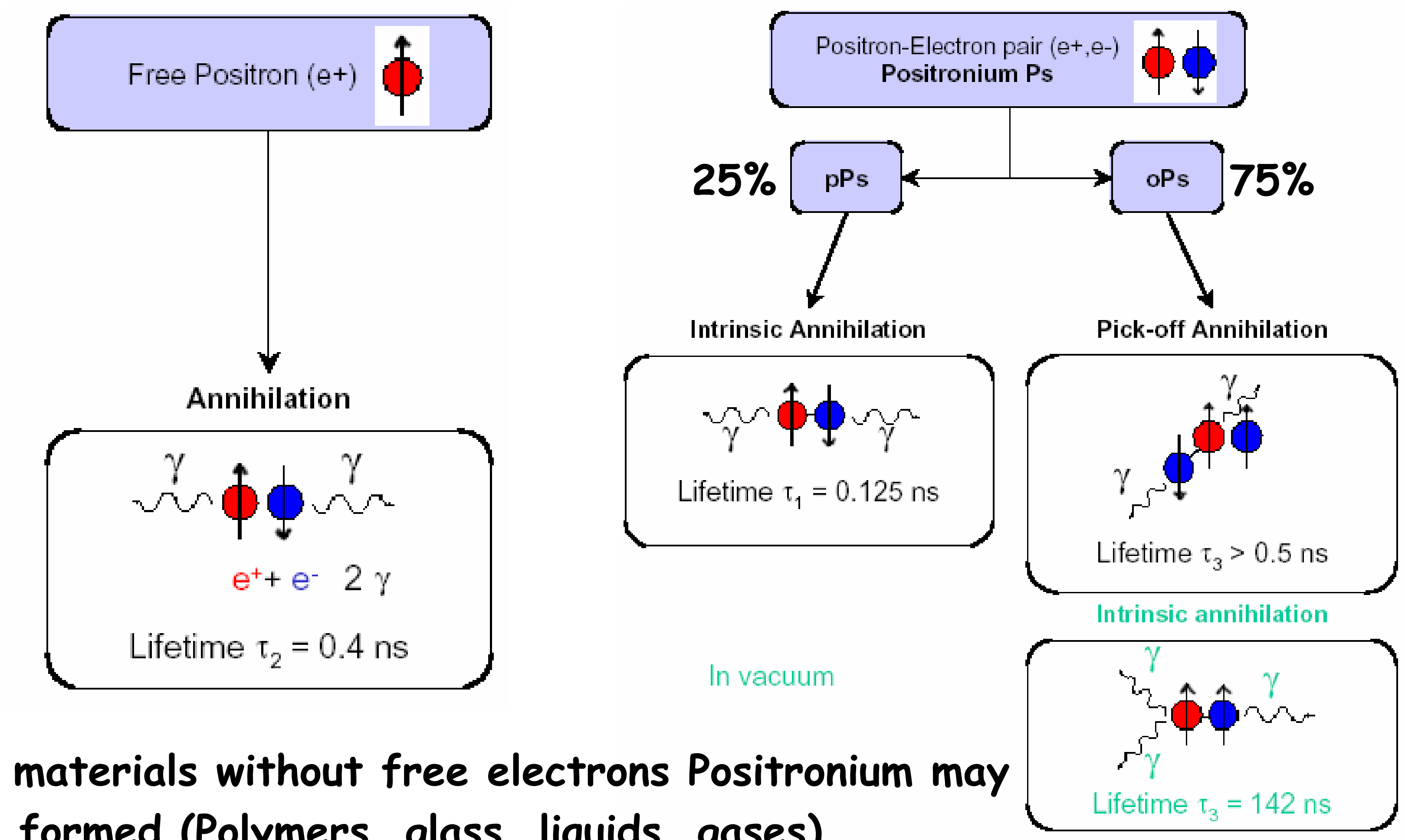
- Lifetime increases due to smaller electron density in open volume

Principles of PALS



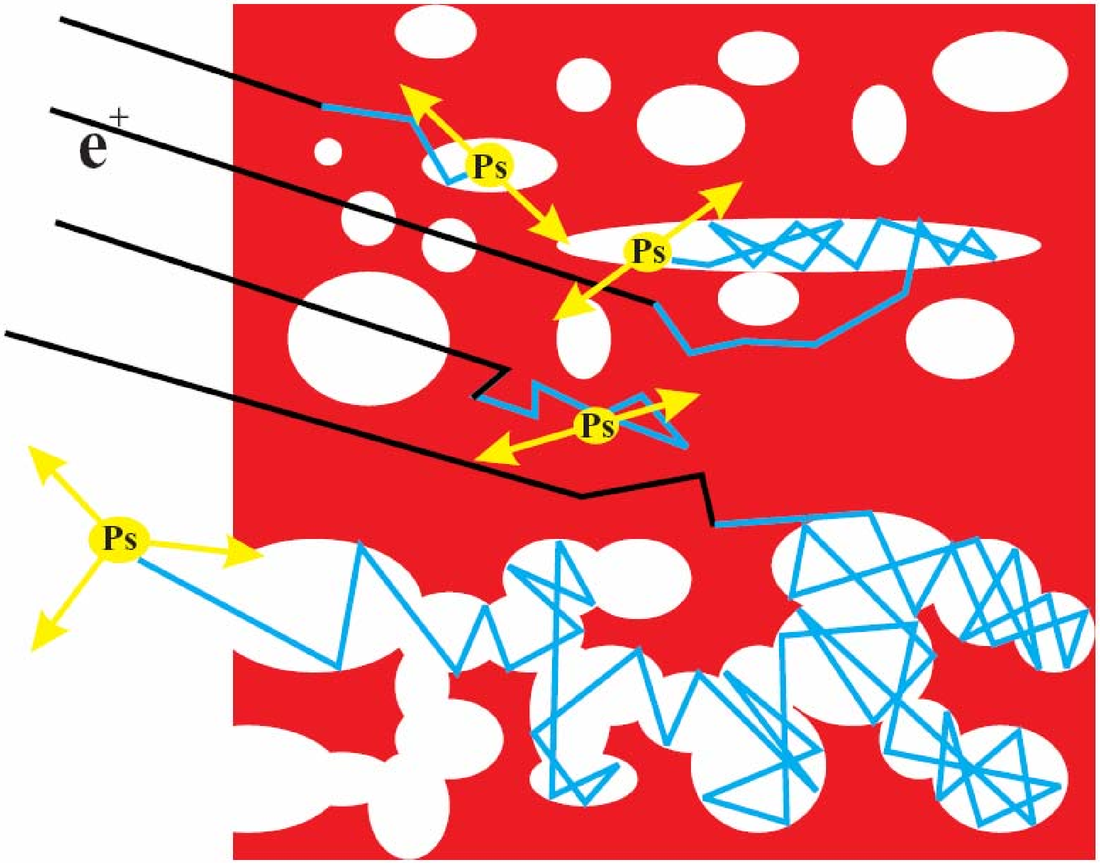
- **Positron lifetime: time between 1,27 MeV and 0,511 MeV quanta**

Principles of PALS: ortho-Positronium



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

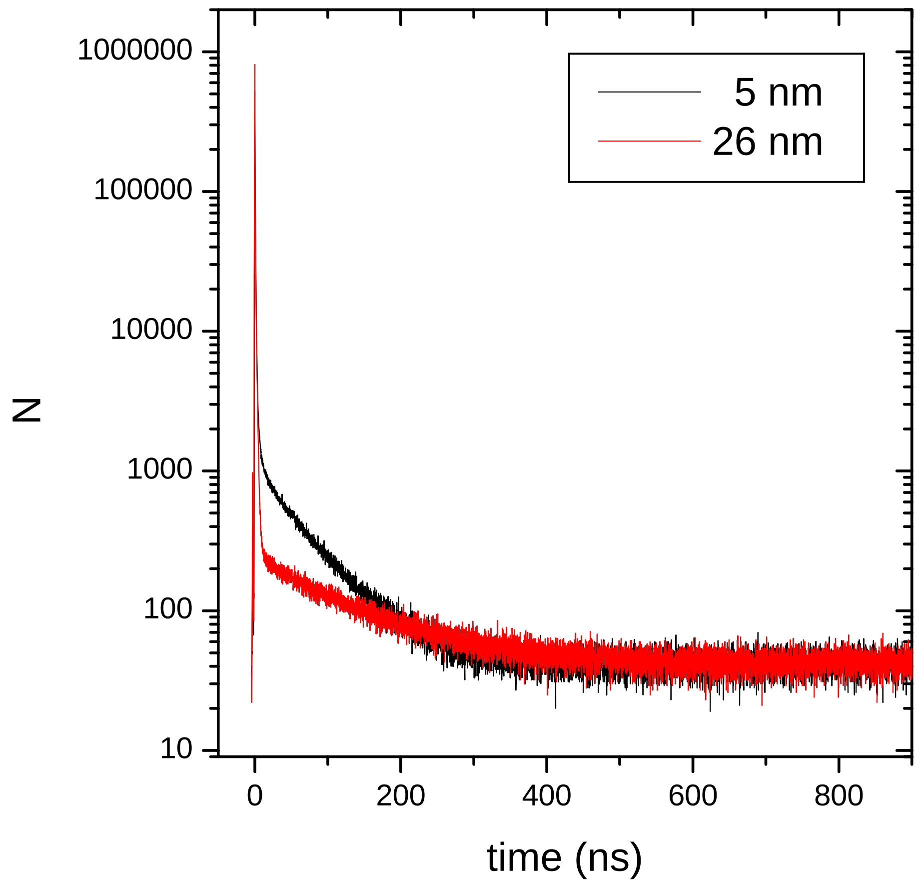
Principles of PALS: pick-off annihilation



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 0.5 ns ... 142 ns
- lifetime can be extracted from spectra

Principles of PALS: typical spectrum

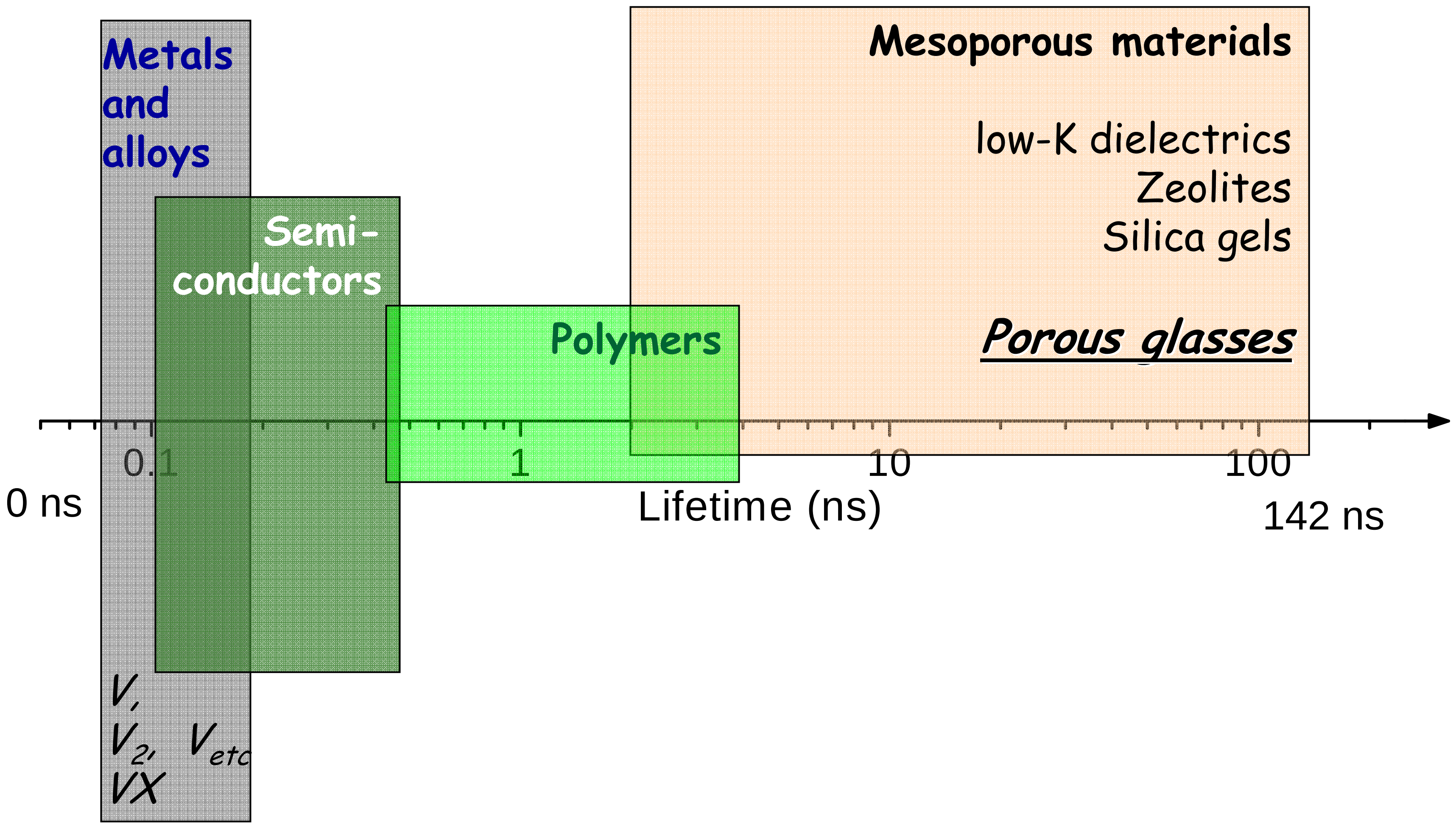


typical lifetime spectrum for porous glass:

- 4 exponential decay components
- p-Ps -> 0.125 ns
- free positrons ~ 0.5 ns
- o-Ps in amorphous region of glass ~ 1.5 ns
- o-Ps in pores

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

Principles of PALS: typical lifetimes



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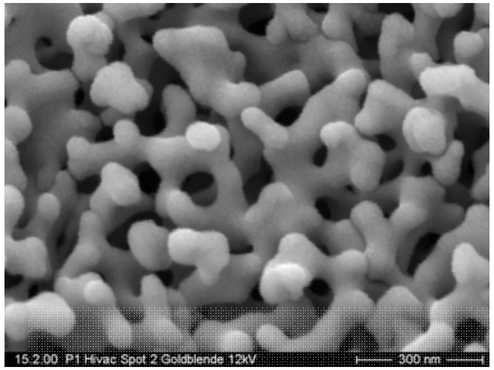
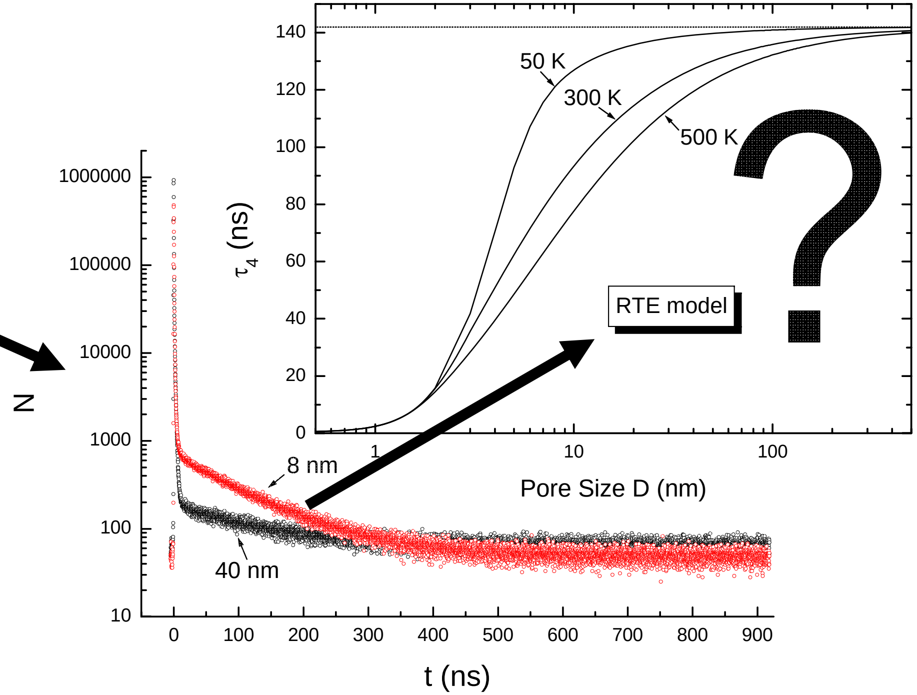
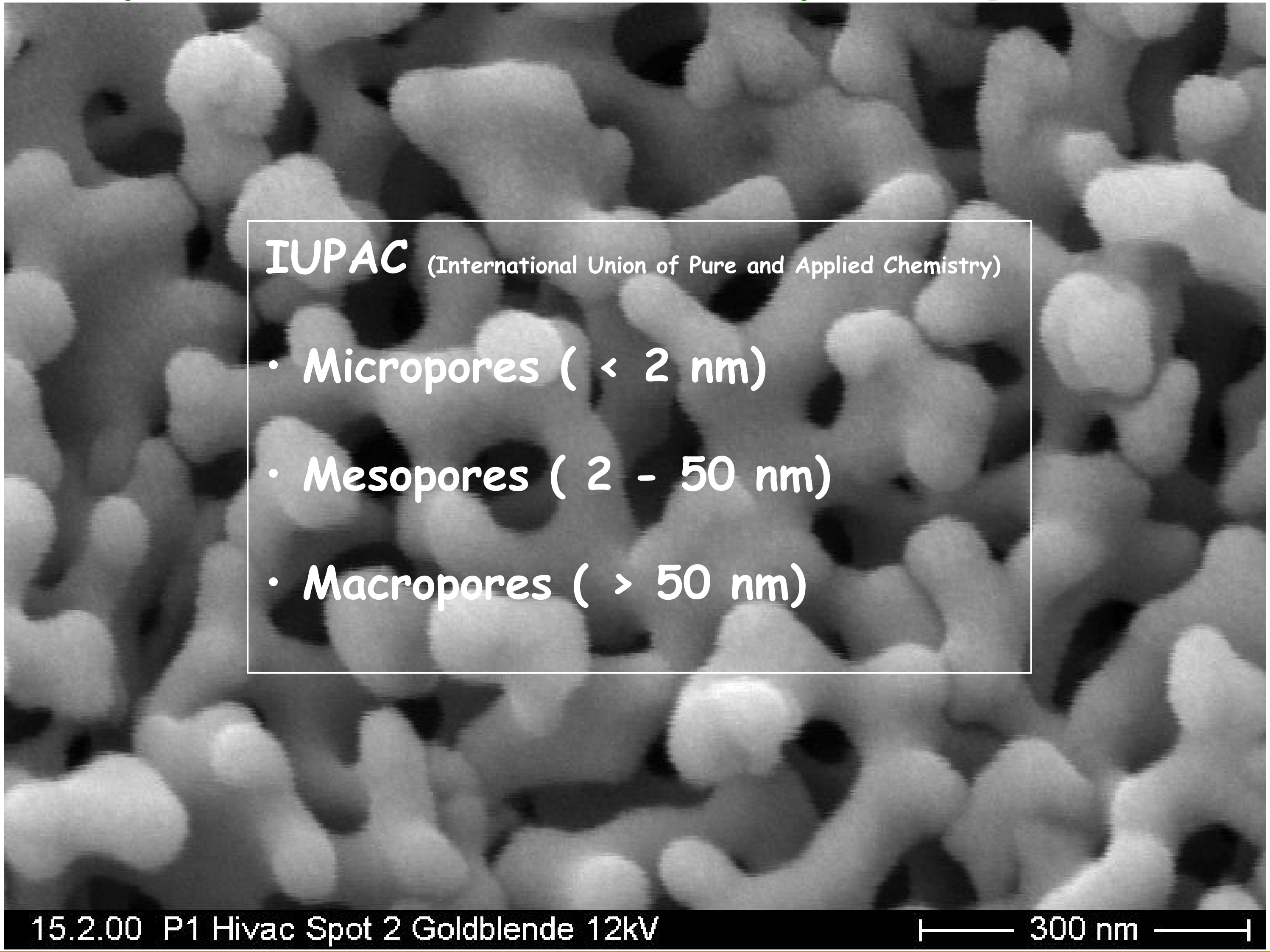
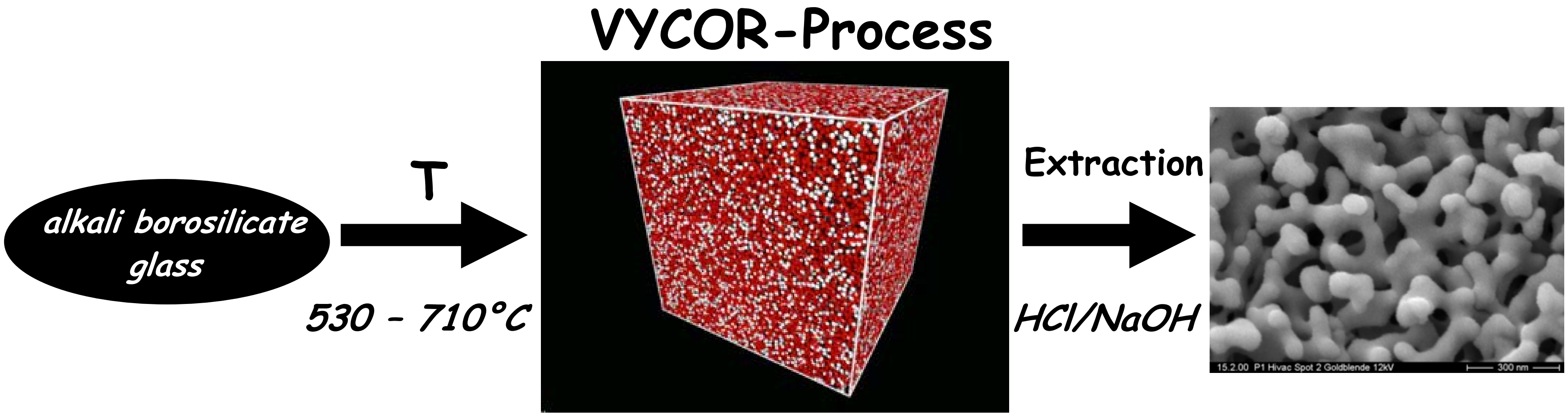




Mesopores - Controlled pore glasses



Controlled pore glasses - CPG

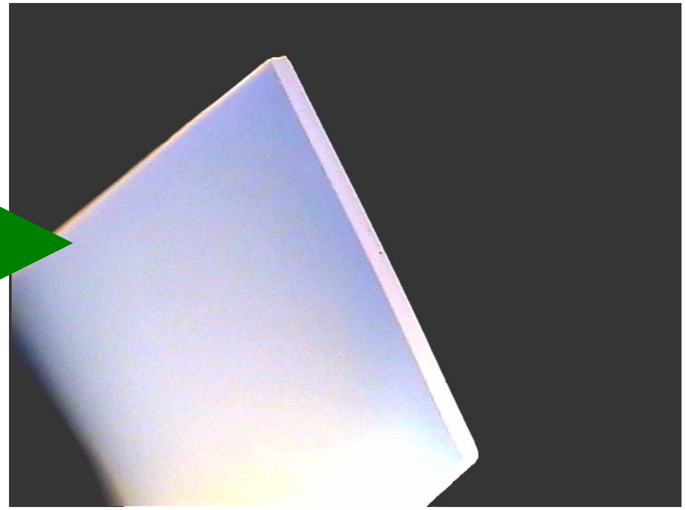


d_p 1 to 110 nm

- spinodal phase separation
- decomposition is initiated by heat treatment
- alkali rich borate phase <-> pure silica
- alkali phase soluable in acid -> silica network
- pore size depends on basic material
- shape depends on duration and T of heat treatment

F. Janowski, D. Enke in F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), *Handbook of Porous Solids*, WILEY-VCH, Weinheim, **2002**, 1432-1542.

Controlled pore glasses - CPG



porous microspheres:

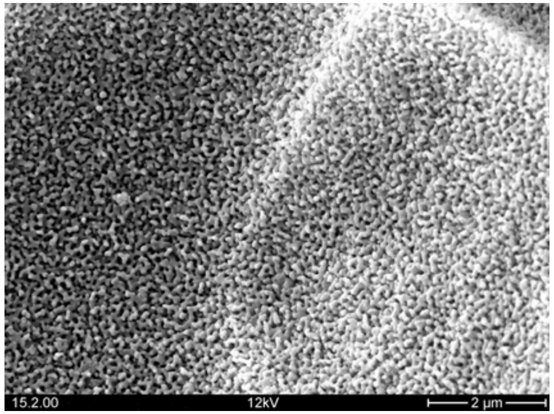
- 100 μm

porous membranes:

- 20 x 20 x 0.2 mm

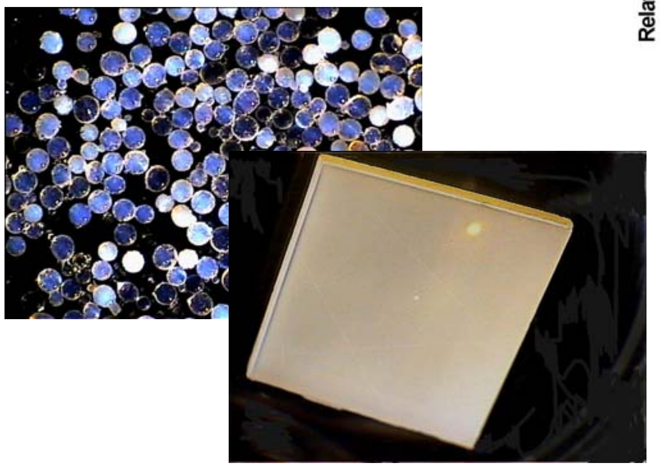
DE-Patent 19848377 A1

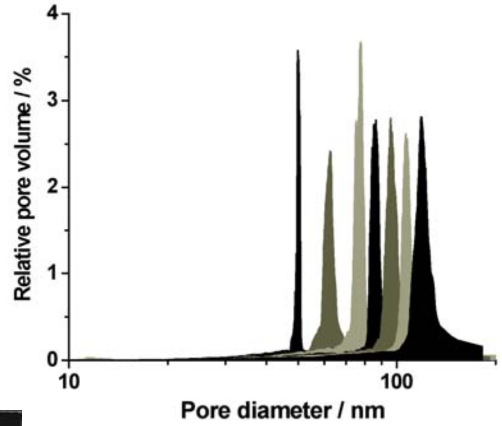
Controlled pore glasses - CPG



- **homogenous microstructure**
- **small pore size distribution**

- **different geometries possible**





- **pore size arbitrary**

D. Enke, F. Janowski, W. Schwieger, *Microporous and Mesoporous Materials* **2003**, *60*, 19-30.

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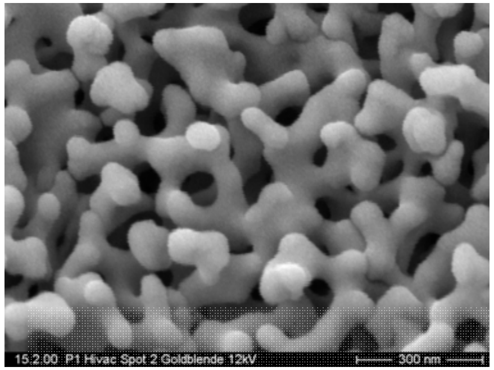
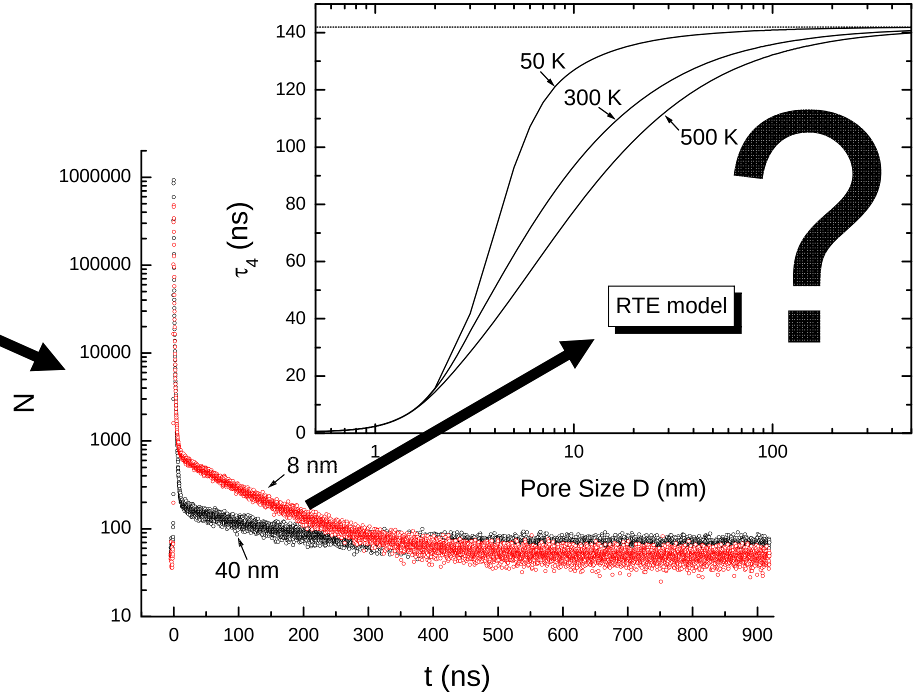
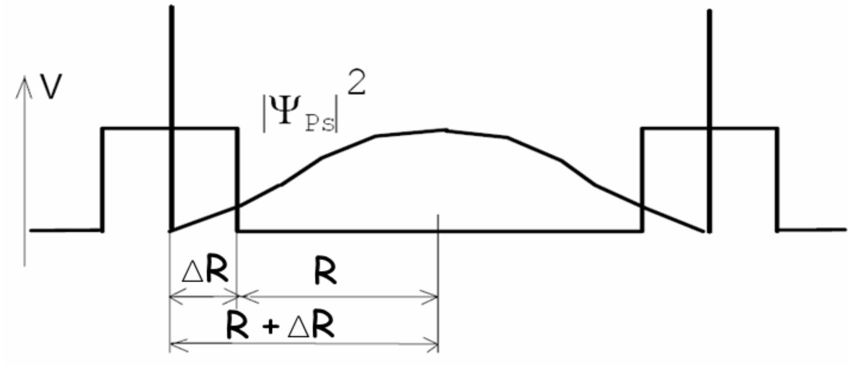




The TE model



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

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

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

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

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

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

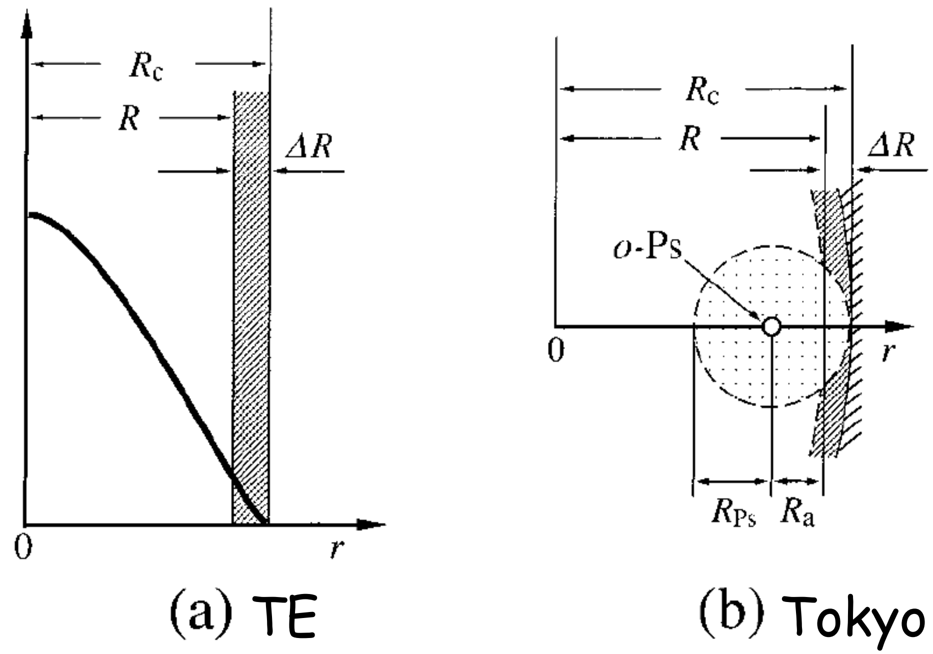
- **ΔR = 0.166 nm determined by Eldrup and Jean**
- **Pore size > 1 nm -> $\lambda_{3\gamma}$ can not be neglected, temperature dependence of o-Ps lifetime (excited states)**

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

  - <u>**Problems:**</u> **- no explicit temperature dependence**
    - two free parameters to be determined



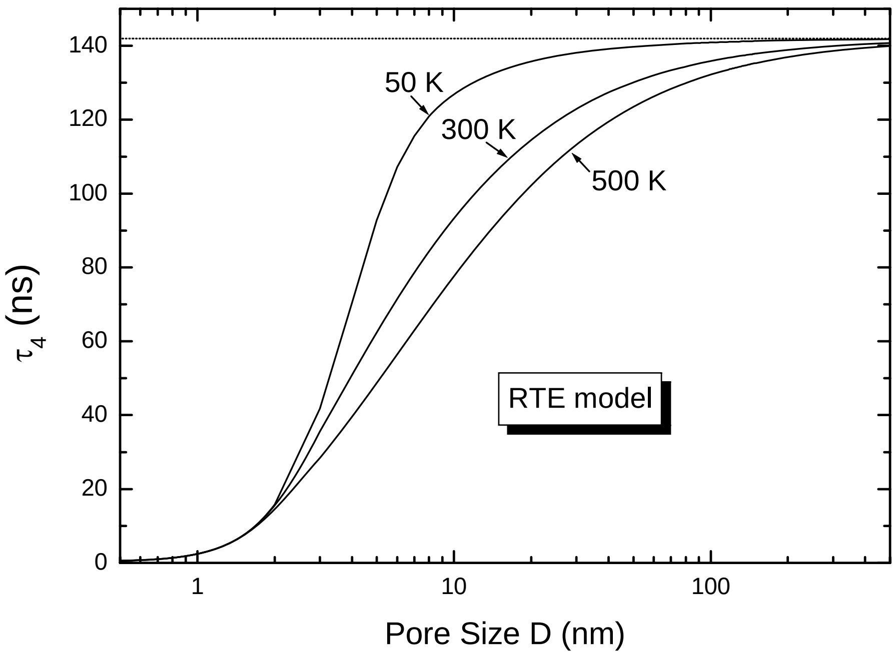
empirical:
R_a = 0.8 nm
b = 0.55

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.

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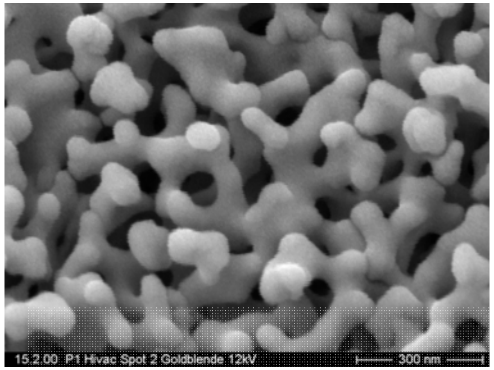
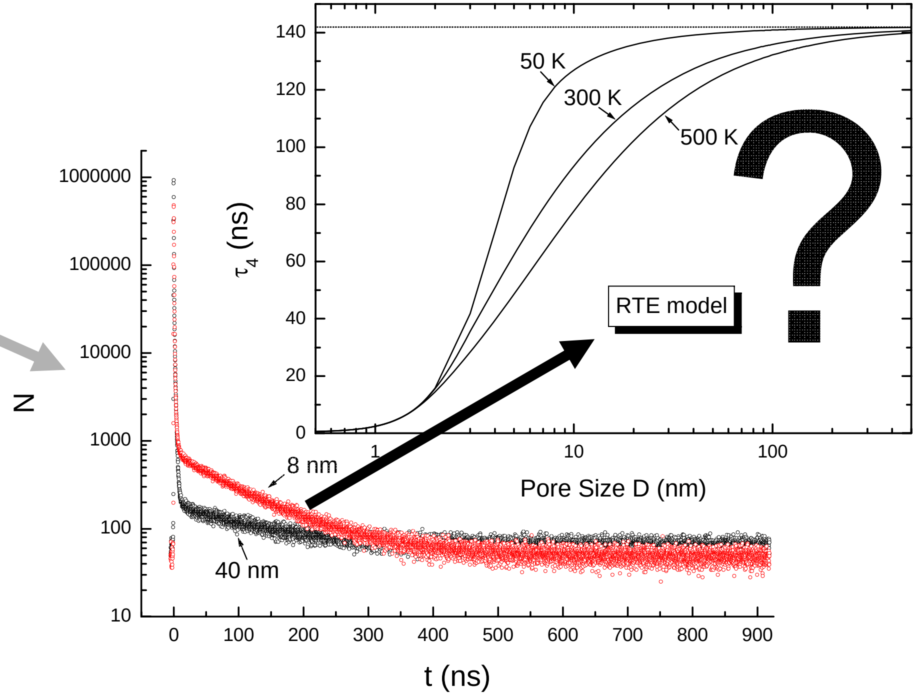
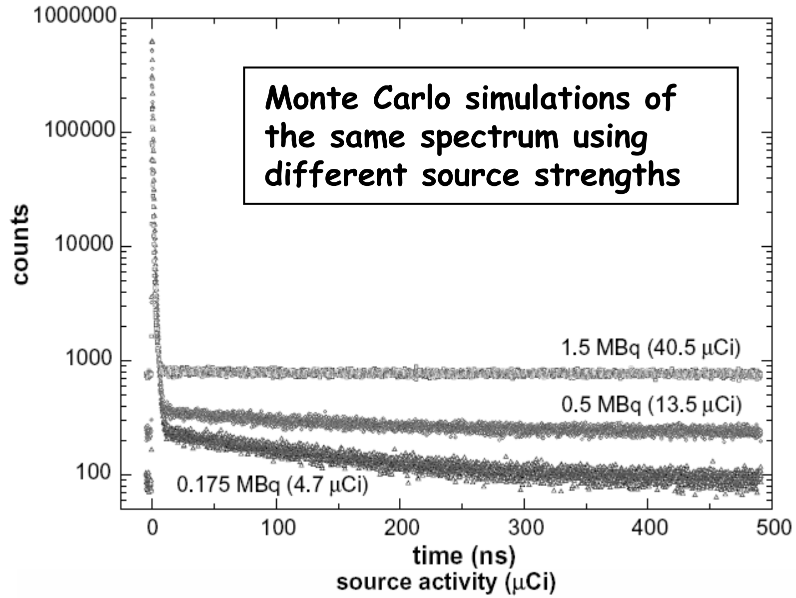


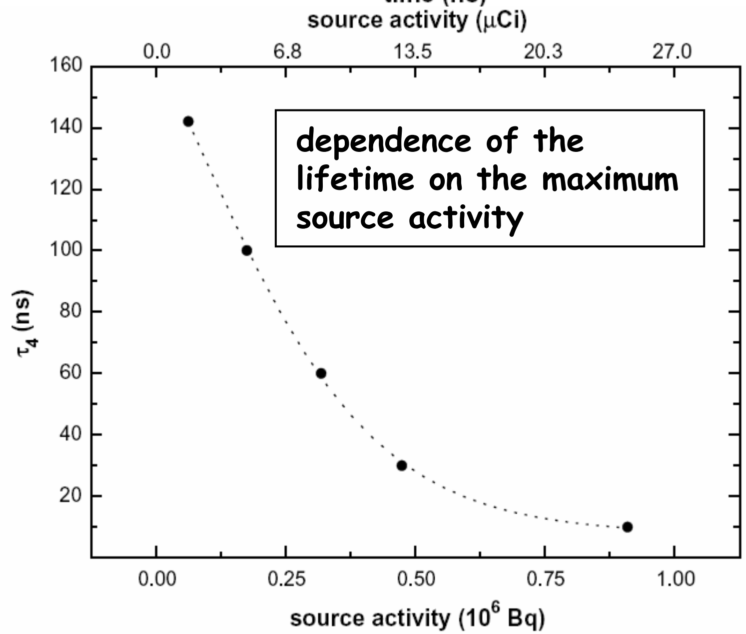


The experiments

- **Important: weak source required to obtain o-Ps lifetime properly (long lifetime component disturbed by chance coincidences)**



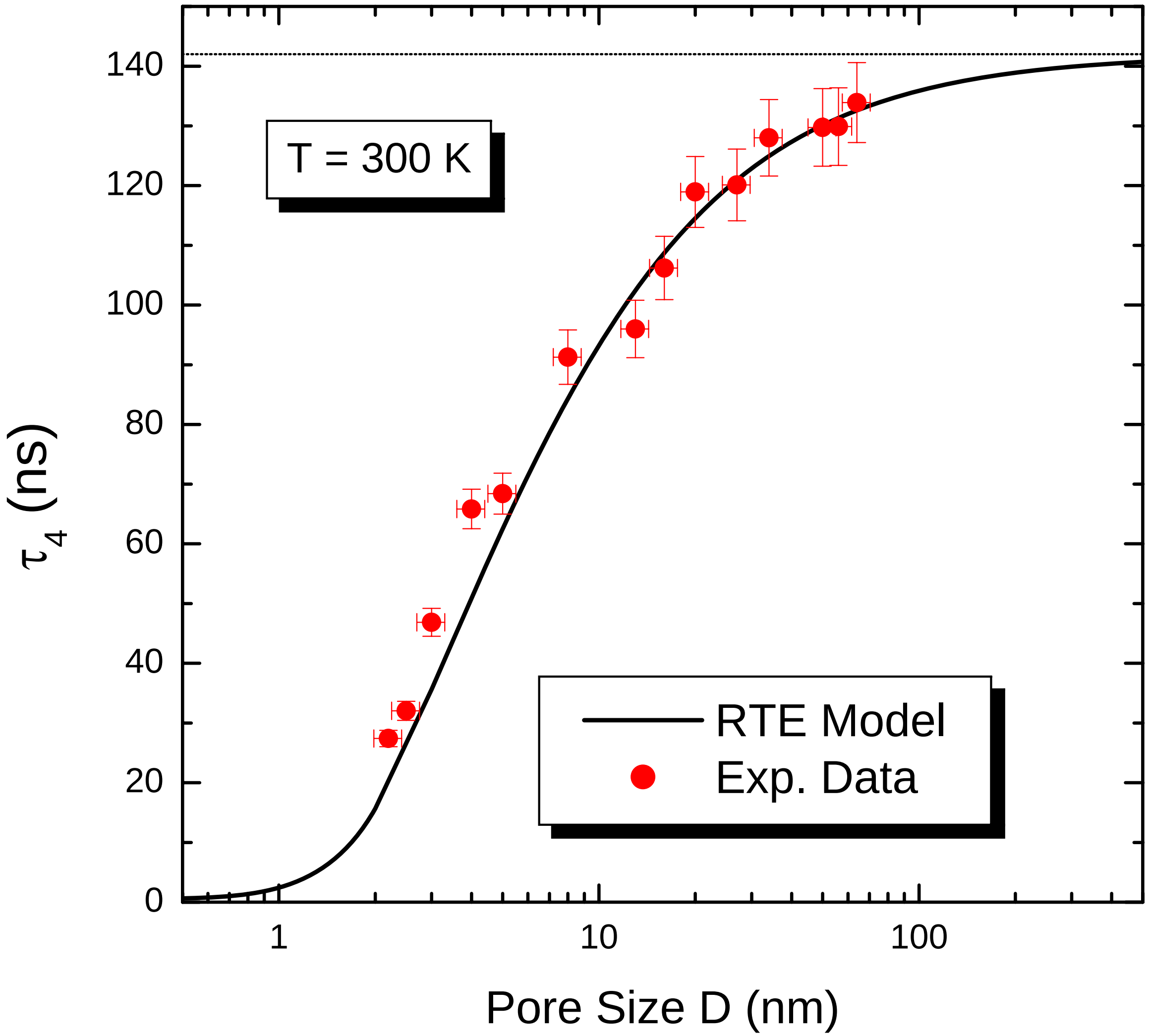
- **When expecting a lifetime of e.g. 120 ns -> max. source strength of 3 µCi recommended**



- **At first measurements at T = 300 K on different pore sizes**

S. Thraenert, E.M. Hassan, R. Krause-Rehberg, *Nucl. Instrum. and Meth. B* **2006**, *Vol. 248 No. 2,* 336.

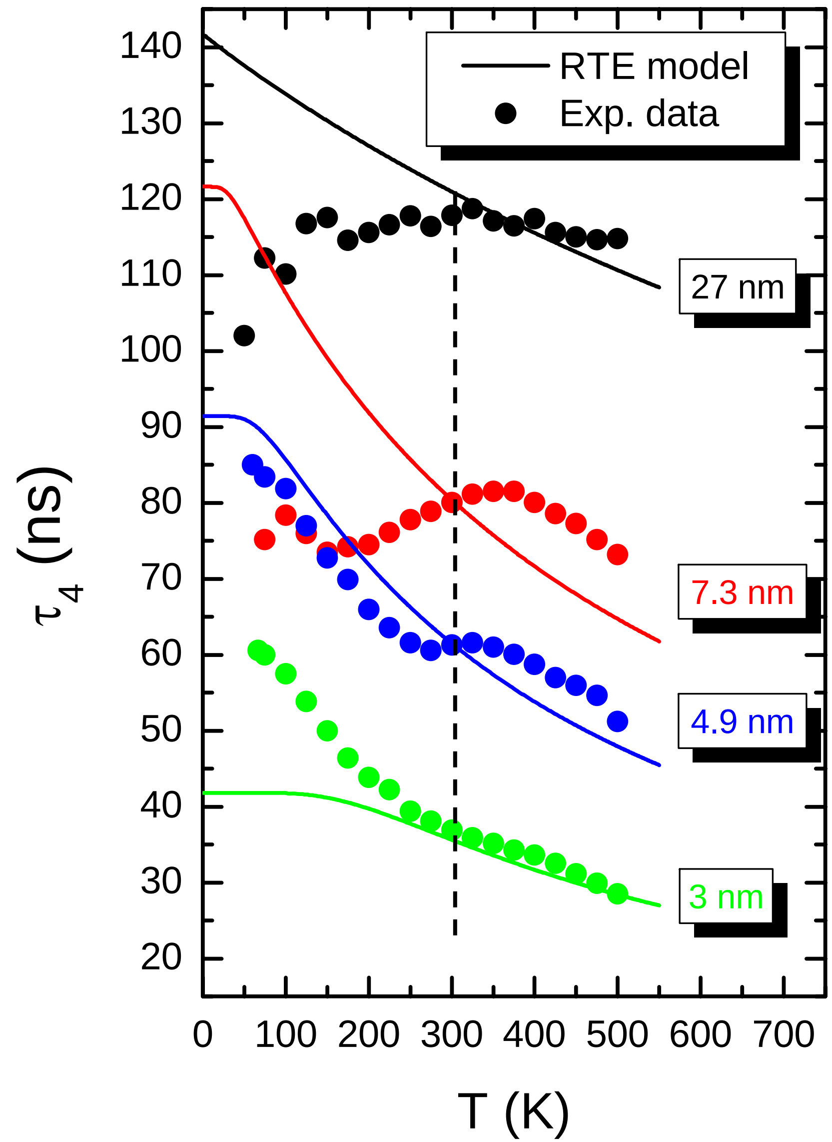
The experiments at T = 300 K



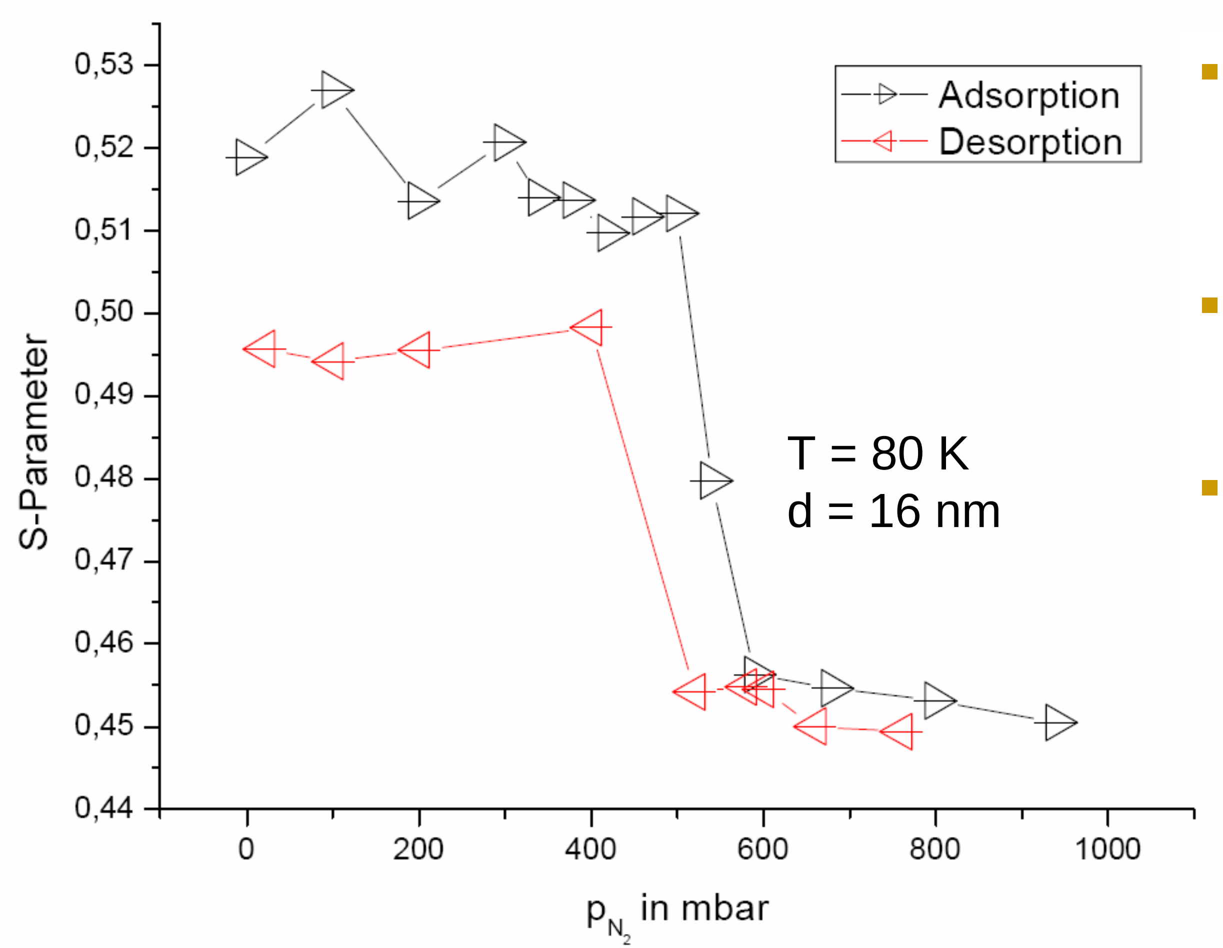
- we measured porous glass in a broad pore size range
- pore size obtained by N_2-adsorption method
- for T=300 K general agreement to the RTE model
- calibration curve for the correlation of o-Ps lifetime and pore size

The T-dependence

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

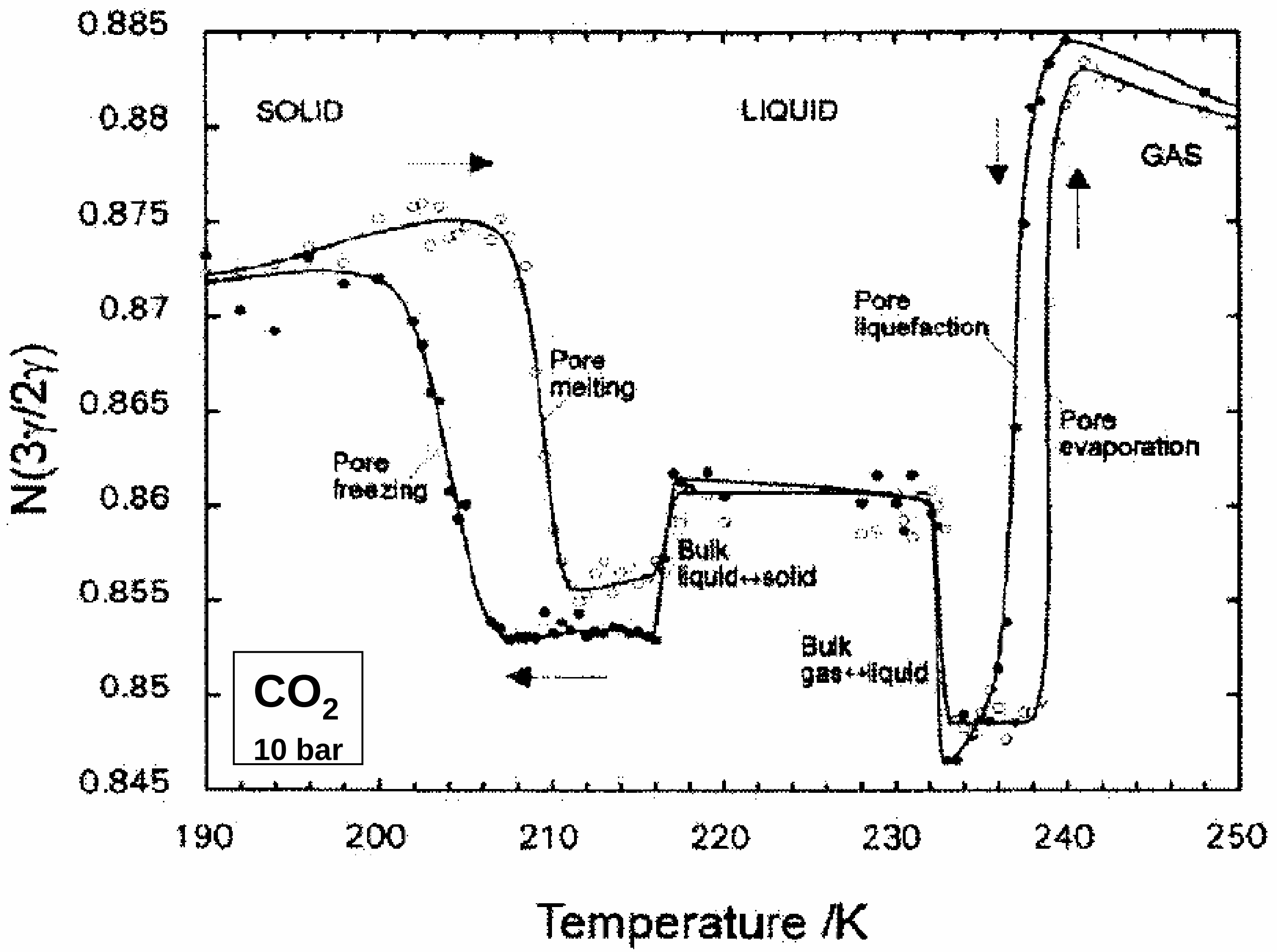


Cryo-condensation in nano-pores



- **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**

Cryo-condensation in nano-pores



- **N-parameter: ratio of 3γ and 2γ annihilations**

J. A. Duffy, M. A. Alam, *Langmuir* **2000**, *Vol. 16.*, 9513-9517.

Summary

- for T = 300 K general agreement to the RTE model -> at room temperature, PALS is a useful porosimetry tool!
- for T > 300 K still acceptable agreement to the RTE model.
- for low temperatures the measurements show disagreement to the RTE model

- Advantages:
  - very sensitive method for small pores (1 nm to 10 nm)
  - also encapsulated pores can be measured
  - non-destructive method