

POSSIBILITIES OF POSITRON ANNIHILATION TECHNIQUES IN THE STUDY OF POROUS SOLIDS AND ZEOLITES

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INTRODUCTION

In the last three decades, positron annihilation spectroscopy (PAS) established itself as a routine method for structural studies of ordered substances. The basics of PAS [1-3] are simple, positrons, antiparticles of electrons and electrons „annihilate“ together, i.e., they disappear from the particle state and gamma radiation is created instead, which can be detected easily. The lifetime of positrons in condensed media varies from 0.1 ns to 0.5 ns, depending on the density and accessibility of electrons available for annihilation. This so-called „free annihilation“ features dominantly the emission of two 511 keV quanta, whereas the 3γ -annihilation becomes important only when the positron and electron form a bound system, positronium (Ps). In fact, Ps can be regarded as the lightest (instable) H-isotope, giving rise to Ps-chemistry. The triplet state, orthopositronium (o-Ps) has a vacuum lifetime of 142 ns, decays via 3γ -emission, whereas the singlet state parapositronium (p-Ps) decays with 2γ -emission and 0.124 ns lifetime. The applications of PAS include both the observation of the fate of positrons (also, because free positrons might get trapped in structural imperfections allowing a unique probe of low-concentration structural defects and the observation of defect pattern evolution) and the use of Ps as a probe. After the discovery of Ps-formation in solid crystalline powders [4] it took several years till broader interest was paid to this “exotic” phenomenon. It was gradually recognized that this occurrence could be exploited on one hand for basic studies on Ps and on the other hand for the development of a novel method for direct and indirect bulk and surface studies of structural imperfections and impurities, observing long-living states connected to o-Ps interactions or trapping of o-Ps in structural and extra-structural volumes acting as trapping centres. Applications of the o-Ps probe for the characterization of nano and mesoporous solid materials through positron lifetime spectroscopy became popular. Such studies take advantage of the fact that, after being formed on a picosecond time scale, o-Ps becomes rapidly trapped in open spaces inside the solid matrix and decays therein. Whereas o-Ps decays in vacuum intrinsically by 3γ -emission, its extrinsic decay in matter due to the interactions with electrons from the surrounding medium is governed by the overlap of the positron wave function with that of electrons, resulting in a 2γ -emission process (pick-off) with a shortened lifetime as compared to the vacuum value for o-Ps. The actual o-Ps-originated lifetimes can range from about 0.6 ns in compact lattices up to 142 ns in vacuum. The simple quantum-well model [5, 6] -correlating the actual o-Ps lifetime to the size of the trapping sites- was applied with remarkable success. This model has been developed further (extended also to non-spherical geometries [e.g., 7, 8]). The “effective size” of the free volumes (whether spherical, cylindrical or cuboid) is correlated with the resulting lifetime of the o-Ps, thus providing a unique method to calibrate positronium trapping sites (structural or extrastructural free volumes) in the nanoscale range (0.1–10 nm). Also, ab initio calculations have been started to estimate the free volumes [9]. The o-Ps trapping equations have found successful applications in various materials featuring intrinsic (molecular) or extrinsic defects (including mesopores), or free volumes in polymers [10]. Such trapping centres could be the cages, voids, channels in the porous solids, e.g., grainy ionic crystals and zeolites. In samples where several distinct types of possible trapping centres exist (various forms of unoccupied places), distinct lifetime components could be expected.

However, in some cases, long lifetime values much exceeding the values corresponding to the known structural free volumes were found. Up to five different lifetimes may appear, from 0.12 ns up to 140 ns, with intensities of the longest components as high as 30%-40% [11-13], the origin of the various lifetime components is, however, somewhat unclear. The high-intensity long lifetimes make data evaluation and interpretation a challenging task. Attention gets drawn necessarily to the validity of data and extracted results, especially as the spread of data referring to nominally identical samples surpasses other examples substantially. Differences between the actual status of samples, differences in the experimental settings of the PA spectrometers and also differences between the data evaluation tools could be assumed as probable causes for that large data scatter. It has been found that, indeed, in addition to the sample synthesis [e.g., 14, 15] and treatment (e.g., degassing of adsorbed water [e.g., 16]), possible changes in the $3\gamma/2\gamma$ -ratio (due to e. g., interactions of o-Ps with any additives present -surface-bound ions, gases, etc.,- which shorten the o-Ps lifetime and increase the 2γ -annihilation) may also strongly and nonlinearly influence the PAS parameters. For recording the 3γ - decay with high efficiency and without distortion, special efforts are needed [17, 18]. The determination of the true LT intensities requires a correction with ρ , the ratio of the $3\gamma/2\gamma$ counting efficiencies [e.g., 17-19]. Those attempts led to the conclusion that the positron annihilation pattern is probably dominated by a near-saturation level trapping of positrons and o-Ps as well [20].

This work reconsiders reasons for large discrepancies in PAS results and presents some selected examples, explanations based on our own data and also an outlook.

EXPERIMENTAL

Among the conventional PAS techniques, positron annihilation lifetime (PAL), Doppler Broadening (DB) technique, the recording of the full energy distribution (FED) of the annihilation radiation and the Extended Doppler Broadening (XDB) technique were used, employing low-activity (0.5-2 MBq) ^{22}Na positron source sealed between thin Kapton or Ni foils. Two fast-fast coincidence PAL spectrometers were employed with appropriate energy window selection for high efficiency recording of the 3γ -events. The DB spectrometer featured an ORTEC HPGe detector (1.2 keV resolution at 497 keV). The measuring chains both on the PAL and on the DB spectrometer consisted of standard ORTEC, CANBERRA and TENNELEC units. Data recording took place with computer-based multichannel cards, the MCA types employed were 4k KFKI RMKI and 16k Oxford Microfast products. Time calibration values from 20.1 ps/ch up to 200.3 ps/ch were used for short or long time range settings, respectively. The PAL spectra contained at least 2.3×10^6 integral counts, the DB spectra had appr. 1×10^6 in the 511 keV peak.

Evaluation of the LT spectra was carried out using the LT v.9 fitting program [21]. The DB spectra were analyzed in terms of the S and W shape parameters and the usability of S-W plots [22] was also considered. However, those parameters have only restricted validity for samples with high 3γ -annihilation fraction. For the characterization of the $3\gamma/2\gamma$ fraction, full γ -energy measurements were also performed (energy range: 40 keV - 1.4 MeV), monitoring the 2γ - and 3γ -annihilation channels with counting the 1.28 MeV photopeak.

As samples, several zeolites were included, not all will be discussed here. Special care was taken to select well-characterised samples with known high Ps yield. The MFI silicalite-1 and mordenite samples were produced in Mulhouse (Lab. Mat. Minéraux, URA CNRS 428, Mulhouse, France) and in Budapest (Centr. Res. Inst. for Chemistry, H-1525, Budapest, Hungary), the Na-Y and Na-X samples were purchased commercially (Grace), the gel-ageing

technology was applied in Zagreb (Div. of Mater. Chem., Ruder Boskovic Inst., Zagreb, Croatia). Besides thermogravimetry measurements, structure characterization of the samples was performed using X-ray diffractometry and NMR-spectrometry. The grain size of the samples varied from about $30 \times 10 \times 10 \mu\text{m}^3$ for the silicalite-1 down to 1-5 μm grain size diameter for Na-Y.

The zeolite powder was pressed (by 0.3 GPa) into disks of 8-13 mm diameter and 1-1.5 mm thickness. The sample sandwich with the positron source was inserted into a holder tube, evacuated but for the study of the influence of gas filling, several samples were measured in gas atmosphere charging the tube with atmospheric pressure nitrogen or argon at room temperature. The temperature dependent studies (e.g., water removal from the mordenite and Na-Y-zeolite, capillary condensation, etc.) were carried out in the 90-430 K range with a cryostat-oven. The influence of various production processes on the sample preparation was studied comparing gel-aged and recrystallized samples, too.

A good reproducibility of the PA results was found by re-recording spectra after months and also when completely reprocessing the samples and repeating the experiments.

RESULTS AND DISCUSSION

LT measurements for the various zeolites show the presence of very long components, exhibiting temperature dependent changes as well as shown for the MFI silicalite-1 (Fig. 1a). The drastic decrease in the long lifetime contribution and the shortening of lifetimes could be ascribed to capillary condensation. Impressive long lifetimes could be observed also for samples produced in Zagreb. It is an unexpected finding that the gel-aged samples may exhibit higher long lifetime contribution as found in crystallized state (Fig. 1b.).

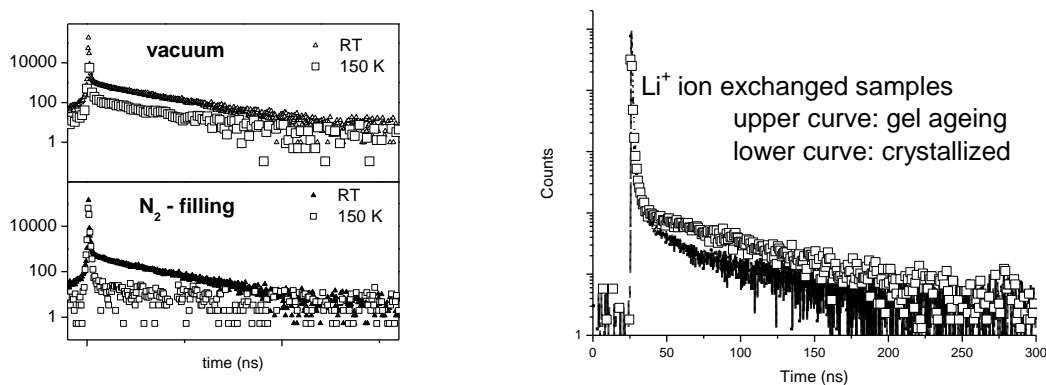


Figure 1. (a, left side) LT distributions for MFI silicalite-a samples recorded in 800 ns range in vacuum (*upper half*) at room temperature and at 150 K and in atmospheric pressure N₂ filling (*lower half*) at room temperature and at 150 K (b, right side) LT spectra recorded in 300 ns for Li⁺ ion exchanged aluminosilicate samples in gel-aged and crystallized state.

LT deconvolutions resulted in up to 5 lifetime components (τ_i) with non-negligible relative intensities (I_i), 0.2-0.5 ns combining the p-Ps and free annihilations, 1-4 ns for o-Ps trapped in microvoids of the lattice, 10-90 ns for o-Ps decaying in channels of the zeolites and 100-135 ns for o-Ps decaying probably in mesopores and outside of the crystallites, in the intergrain space. A selection of results is presented in Table 1, showing a strong influence of absorbed water on the LT data. Without going into details [17-20, 23] the complexity and absolute importance of intensity corrections must be mentioned here.

Table 1. LT data (lifetimes and relative intensities from the four component evaluation) on zeolite samples at room temperature in vacuum or in gas filling or in dry air (τ_i lifetimes are given in ns, I_i intensities in %, total intensity is 100%, relative errors are 3% in average).

Sample	τ_1	τ_2	τ_3	τ_4	I_1	I_2	I_3	I_4
silicalite-1 (vac.)	0.47	2.28	22.3	133.2	44.3	24.4	2.6	28.7
silicalite-1 (N ₂)	0.50	1.9	22.5	108.9	46.7	19.9	4.0	29.4
silicalite-1 (Ar)	0.46	2.1	20.5	74.9	47.7	21.9	5.1	25.3
Na-Y (air)	0.21	0.4	1.0	1.8	21.0	70.9	5.1	3.0
Na-Y (vac.)	0.40	2.2	15.2	110.2	44.2	23.2	11.4	21.2
Na-Y (dry)	0.17	0.4	1.1	2.2	15.4	62.6	7.7	14.2
PtFe-Y (dry)	0.20	0.4	1.5	3.2	21.2	63.4	6.4	8.9
ZSM-5 (dry)	0.24	0.5	1.5	3.9	22.1	73.3	3.7	1.0
PdFe-ZSM-5 (dry)	0.18	0.4	1.2	2.3	22.7	59.6	12.6	5.1
Na-X (dry)	0.18	0.4	1.2	1.9	16.6	61.6	10.5	11.2
PdFe-X (dry)	0.16	0.4	0.9	2.0	15.5	75.6	5.9	2.8

It seems that degassing and evacuating the samples makes the long lifetimes first really visible. This effect was also studied by DB measurements and it has been pointed out that the conventional setting of energy windows just at the 511 keV peak is not sufficient for appropriate scaling of the 3γ -contribution, for this task regions far from the 511 keV peak should also be recorded and processed.

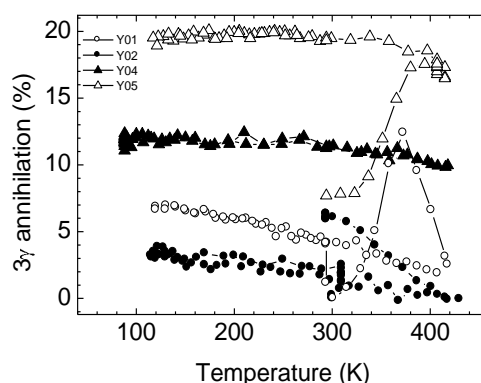


Figure 2. Water degassing of various Na-Y and Na-X zeolites during vacuum heating (started from 300K and cooling down the samples after the peak temperature to cca. 100 K).

As demonstrated in Fig. 2., the conventional S-parameter description would not point to the complexity of the procedure as shown in the $f_{3\gamma}$, the 3γ -fraction in the annihilation spectrum, i.e., this is the „survival portion“ of the o-Ps atoms. It is also indicated by these results that the combination of LT and DB improves the power of PAS a lot and combined multi-parameter plots should be used whenever possible. These results point also to the need of caution with respect to trapping center dimension values as one has to be sure about the validity of experiments. This point deserves a detailed discussion [e.g., 19, 20, 23] which, however, exceeds the limits of this paper.

CONCLUSION

PAS investigations of porous media (zeolites) request special attention with respect to the sample selection (including the production technology as well) and the tight control of the physico-chemical conditions. For LT studies the experimental conditions must be specifically tuned for the as-full-as-possible recording of the events with respect both to the energy and the time windows. This could be best obtained recording the full event distribution setting energy and time limitations of the “start” and “stop” signals only off-line, i.e., 3γ -contribution and 2γ -contribution could be separated this way [24]. It could be also concluded that for LT measurements the most critical requirements are the selection of a long-enough time range to accommodate even the longest component with sufficient additional range allowance for the determination of the background and the efficiency corrections for the relative intensities, otherwise the branching of various components could be estimated incorrectly. In addition to extensions of the by now “traditional” PAS studies on porous materials to newer but still “conventional” questions (like the investigation of the sensitivity of PAS to the preformation of zeolite structure in gel, or the study the radiation damage procedure and extent in zeolites, etc.) at present the interest rises to using the porous systems simply as a medium for high-efficiency production of Ps. Experimental performance optimization is crucial [25] when new terrains are entered and previous data do not exist. As two recent examples the proposed gravitational experiments on antihydrogen [e.g., 26] could be quoted where thin mesoporous silica films yield reemitted o-Ps in sufficient amount [27], and the other advanced project is the study of Ps₂ molecules [28, 29] also in substances which allow high production probability and long survival of positronium atoms.

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