

# PALS investigation of resorcinol under high pressure

Maciej Tydda,  
Bożena Jasińska,  
Agnieszka Pieniążek

**Abstract.** Two kinds of measurements were conducted with resorcinol at high pressure: the first one with the use of a mechanical press and the second one with the use of a gaseous compressor. In the second case, due to some gas penetrating the material structure, the lifetime spectra obtained were difficult to analyze. The free volumes in resorcinol were influenced both by high pressure and the gas coming into the crystallographic structure.

**Key words:** free volume • *ortho*-positronium (*o*-Ps) • pressure • positron annihilation lifetime spectroscopy (PALS) • resorcinol

## Introduction

A positron which penetrates the matter may annihilate directly with one of the electrons, or in some materials, it may also form a hydrogen-like bound state with one of the electrons of the medium, called positronium (Ps). Positronium can exist in two forms (which differ by their total spin value): *para*-positronium (singlet state; *p*-Ps) and *ortho*-positronium (triplet state; *o*-Ps). These sub-states have their lifetime values in vacuum determined at precisely  $\tau_1 = 125$  ps for *p*-Ps and  $\tau_2 = 142$  ns for *o*-Ps [2, 3].

In a condensed matter the lifetime of *o*-Ps can be significantly shortened by the pick-off process, depending on the local electron density of the medium. In such cases a positron bound in positronium can annihilate with one of surrounding electrons. The lifetime of *ortho*-positronium provides information about the size of free volumes (space with a significantly lower electron density in comparison to the bulk material) in the solid state material in which *o*-Ps may locate and later decay by the pick-off process. The relation between the mean lifetime of *ortho*-positronium and the void size is described by the commonly used Tao-Eldrup model [1, 8], which assumes a spherical size of the void. Positron annihilation lifetime spectroscopy (PALS) is an experimental method which makes it possible to investigate the free volumes with no external access. This gives

M. Tydda, B. Jasińska<sup>✉</sup>, A. Pieniążek  
Maria Curie-Skłodowska University,  
Institute of Physics,  
1 M. Curie-Skłodowskiej Sq., 20-031 Lublin, Poland,  
Tel.: +48 81 537 6288, Fax: +48 81 537 6191,  
E-mail: bozena.jasinska@poczta.umcs.lublin.pl

Received: 27 July 2012  
Accepted: 24 October 2012

an obvious advantage in the studies of many classes of materials, especially the porous ones, comparing to the adsorption/desorption techniques.

The lifetime spectra also provide information about the intensities of the respective components. The *o*-Ps intensity depends on many factors such as radicals, the presence of active groups or temperature. In this case it is a measure of the free volumes accessible to positronium formation, no other effects were found in previous studies concerning resorcinol [4, 5].

Earlier studies indicate that PALS may be a useful technique in investigating free volumes in benzenediols [4], because it showed, for example, the changes of the *o*-Ps lifetimes and intensities in free volumes as a function of temperature. A transition between two solid state phases in resorcinol was also observed [6].

The aim of this study was to observe the behaviour of free volumes in resorcinol at high pressure exerted by a mechanical press or by a gaseous compressor, with a possibility of the gas penetrating the material.

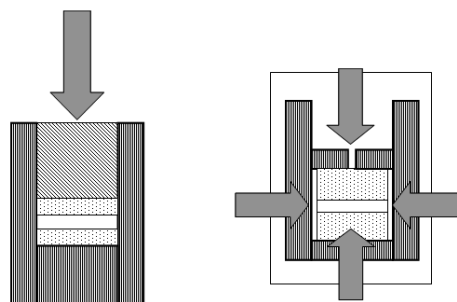
## Experimental

The material under investigation was resorcinol – one of the organic compounds in which two hydroxyl groups are substituted onto a benzene ring. There exist three isomers of the investigated material: catechol (benzene-1,2-diol), resorcinol (benzene-1,3-diol) and hydroquinone (benzene-1,4-diol). All of the compounds are colorless, and at room temperature remain in a solid state. Resorcinol may be obtained from melting resin and potassium hydroxide, or synthesized with, for example, the use of 3-iodophenol or phenol-3-sulphonic acid with potassium carbonate. At low concentration it is used in medicine as an antiseptic disinfectant in ointments applied when treating chronic skin diseases, or in medical soaps. Chemistry also uses resorcinol as an intermediate material for the synthesis of other pharmaceuticals or organic compounds and in the production of dyes and plasticizers.

Even though benzenediols are used intensively in the industry and analytics, they remain the subject of studies of numerous scientific papers published over the last 10 years.

Each isomer has a different crystallographic structure [4] and, therefore, a different shape of the free volumes. In catechol and hydroquinone the free volumes have the shape of channels running through the structure. In resorcinol, isolated ellipsoidal voids exist between the molecules. Each of these voids is surrounded by the rings of the material and they are not connected to each other. Resorcinol can serve as a pattern material to determine resistance to gas pressure.

The lifetime spectra were collected at room temperature, using a fast-slow spectrometer with BaF<sub>2</sub> scintillators. The time spectrum was recorded in the range 50 ns, the time resolution of the spectrometer was  $2\tau_0 \approx 0.24$  ns. The total count numbers per each spectrum was about  $3.5 \times 10^6$ . Spectra were decomposed into 3 or 4 components by the LT program [7]. The first component comes from *p*-Ps decay (fixed on 125 ps), the second one can be ascribed to free annihilation of positrons and one or two, the longest-lived ones, to *o*-Ps decay.



**Fig. 1.** Chambers for measurements at high pressure: left – hydraulic press; right – gaseous compressor.

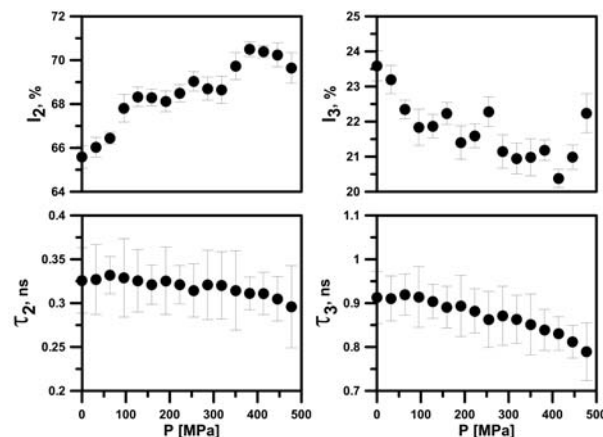
In this paper considerations are restricted mainly to the *o*-Ps components and prioritizes the investigations of the materials under high pressures by a mechanical press or by a hydrostatic gas pressure.

A Unipress U1 gas compressor was used to introduce argon into a chamber holding the sample. The pressure of the gas was changed in the range 0–450 MPa with a step of 30 MPa. A different kind of measurement was made using a hydraulic press with the maximum pressure at about 470 MPa.

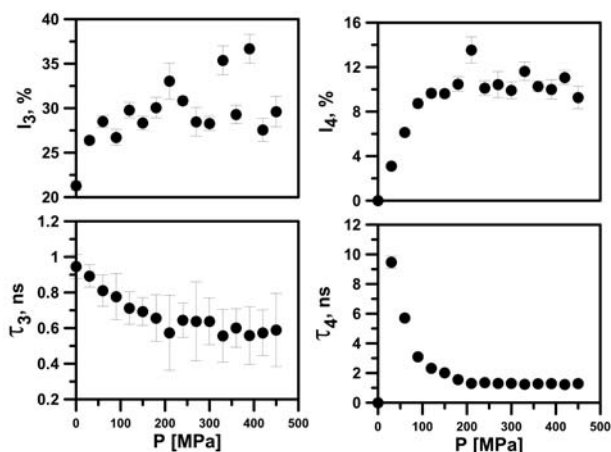
## Results and discussion

The main interest of this paper is the influence that high pressure has on the material, mainly the size of the free volumes. In the first experiment, a sample was placed in the chamber (Fig. 1) where pressure was changed by using a hydraulic hand press. Figure 2 presents the results of free annihilation of positrons in the material ( $\tau_2$ ) and the decay of *o*-Ps ( $\tau_3$ ). In the full range of pressure the measured lifetimes of both components decrease. The  $\tau_2$  value decreases because the electron density in the material increases along with applied pressure which is correlated with the significant intensity growth. On the other hand,  $\tau_3$  decreases with size of the structural free volumes. The third component exists even at the highest pressure, which means that the size of the free volume is still above the low range of positronium trapping.

In the second pressure producing technique, the material was placed in the chamber where gas could penetrate the sample (Fig. 1). While analyzing those measurements, an additional *o*-Ps component (not



**Fig. 2.** The lifetimes and intensities of free annihilation and *o*-Ps decay in resorcinol as a function of pressure (hydraulic press).

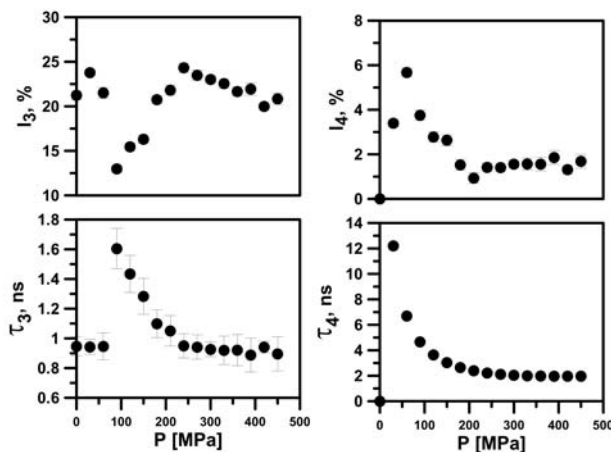


**Fig. 3.** The lifetime and intensity of *o*-Ps components in resorcinol as a function of argon pressure.

visible in previous investigations) was observed ( $\tau_4$ ). The mean lifetime value of this component reaches 10 ns at 20 MPa. It should be interpreted as related to *o*-Ps annihilation in the gas, while the shorter lived *o*-Ps component ( $\tau_3$ ) should be ascribed to the annihilation in the voids of resorcinol.

Figures 3–5 show the dependence of lifetime and intensity of *o*-Ps components on argon’s pressure in the chamber.

An increase of the gas pressure causes shortening of the lifetimes of both components:  $\tau_3$  decreases from 0.9 ns to about 0.6 ns at the pressure of 200 MPa while  $\tau_4$  decreases rapidly from 9 ns to about 1.5 ns in the same range of pressure. Afterwards, both values are almost constant (Fig. 3) and  $\tau_3$  stabilizes on a strangely short value of 0.6 ns. This was one of the reasons why an attempt to apply different methods of spectra analysis has been made. The other one was to separate the components coming from the annihilation in the material and the gas. To perform this task additional measurements of *o*-Ps lifetimes in pure argon, without a sample, were done. The measured values of  $\tau_4$  were described as a function of pressure and interpolated to the required range of pressures. From that function, specific values of lifetimes were found and used in spectra analysis. Results of this analysis are presented in Fig. 4. What could be seen, is a rapid increase of  $\tau_3$  (from about 0.95 ns to 1.6 ns) and the corresponding  $I_3$  decrease



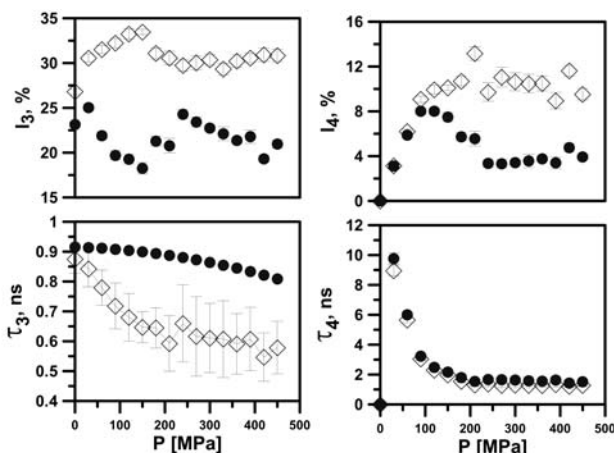
**Fig. 4.** The lifetimes and intensities of *o*-Ps components,  $\tau_4$  values fixed on values obtained for pure argon.

at a pressure close to 100 MPa. This may indicate a destruction of the material and gas penetration into the structure. In the crashed material free volumes can join and in effect their size increases while the number decreases. The step like effect of the changes of the lifetime and intensity of the free annihilation is observed at the same pressure, which confirms such a supposition. This hypothesis, however, must be verified, for example by the X-ray diffraction measurements. From rough measurements, differences in X-ray patterns for the material before and after the pressure measurements are visible.

The intensity of the gas component ( $I_4$ ) is very low in comparison to those presented in Fig. 3. This suggests that the fixed lifetimes of argon are different than the ones which were actually obtained in the experiment. As the lifetime and intensity of the fourth component was significantly different than in the free analyses of the spectra, different methods of analyses have been conducted. In this attempt, data from the measurements made with the use of a hydraulic press were exploited.

Due to that, the values of  $\tau_3$  obtained in the measurements with the use of a hydraulic press were fixed, while  $\tau_2$  and  $\tau_4$  were left free (Fig. 5 filled circles). The fourth component’s lifetime is close to the one obtained in the first attempt (with all components set as free, with the exception of *p*-Ps). Intensity of this component is higher than in the case of fixing  $\tau_4$  values for argon, but lower than in the case of the “free” analysis. This method of analysis also seems to not giving optimal results, since the information about  $\tau_3$  disappears and conclusions may be drawn only from the intensities.

Each kind of the analyses (fixing  $\tau_3$  or  $\tau_4$ ) presented above has been made assuming that in the gas-sample system both media do not interact with each other, but such procedures do not give satisfying results. In the environment like this there is a possibility of forming some kind of complex gas-sample structures. That leads to the conclusion that the only parameter that does not change depending on the kind of measurement, should be applied. This means that the lifetime of positrons in the bulk material related to the electron density should



**Fig. 5.** The lifetimes and intensities of the *o*-Ps component in resorcinol as a function of argon pressure. The lifetimes are fixed on values obtained from the measurements in the hydraulic press. Symbols denote: empty diamonds –  $\tau_2$  fixed, filled circles –  $\tau_3$  fixed.

be the same at the respective pressure. In effect, a fourth kind of analysis has been done. In this last attempt, lifetimes of free annihilation were fixed on values obtained in the measurements made with the use of a hydraulic press. The results are shown as empty diamonds in Fig. 5. The values of lifetimes and intensities of the *o*-Ps components obtained by this method reassemble, in principle, the results of the first analysis, presented in Fig. 3.

### Conclusions

From the two kinds of measurements, one can obtain different conclusions concerning material behaviour under high pressure.

In the experiment done with the use of the hydraulic press it appears that the material was squeezed up to a pressure of about 450 MPa, but was never crushed as the lifetime and intensity of the third component did not change rapidly. In the experiment made with the presence of the gas a few methods of spectra analyses were proposed in order to find the most informative one. From these methods in which some lifetime values were fixed, one can find that the material is crushed somewhere between 100 and 200 MPa and the gas rapidly penetrates the inner structure of the material. To determine the precise point of breaking of the structure

in the presence of the gas a more detailed analysis, correlated with the XRD technique, is needed.

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