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# The connexion between positronium and the condensation of oxygen on silica and alumina powders

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**Abstract.** Positronium annihilation has been related to the condensation of oxygen on silica and alumina powder. Doppler-broadening measurements on the 511 keV annihilation line, together with  $3\gamma/2\gamma$  determinations, reveal the early stages of molecular adsorption. An application of the Langmuir model yields values of 1130 K and 1630 K for the respective adsorption energies.

## 1. Introduction

A positron injected into silica is likely to form positronium (Ps), which will exist in the material as a delocalized exciton-like Bloch state (Dupasquier 1983). In the proximity of a surface a large proportion of the Ps will diffuse and be emitted as a consequence of a negative work function. This has been verified in positron-beam experiments on a single crystal of quartz, which have revealed that Ps is emitted normally in the *c*-direction from a surface as a monoenergetic peak with an energy of 3.26 eV (Sferlazzo *et al* 1987) and by work on amorphous fine particles of SiO<sub>2</sub>, which found a mean Ps emission energy of 0.8 eV (Chang *et al* 1985).

A number of positron studies has been made on porous systems of SiO<sub>2</sub>, which are of technological importance due to their capacity to adsorb gases. In addition to increasing our understanding of positron interactions with gases, the aim has been to explain the behaviour of gases in the specialized circumstances of a constricted space above the solid. Thus measurements have been made with various gases permeating the SiO<sub>2</sub> gel (Chuang and Tao 1974) and Vycor glass (Wilkinson *et al* 1992), each of which presents a large specific area.

In this work we have concentrated on the condensation of oxygen on silica and alumina substrates as a function of temperature. We have employed Doppler broadening measurements on the 511 keV annihilation radiation together with assessments of *ortho* Ps intensity, to reveal the early stages of molecular physisorption. An application of the Langmuir adsorption model allows the determination of the adsorption energies of O<sub>2</sub> in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> powder.

## 2. Positron annihilation spectroscopy

Positrons that annihilate with electrons in SiO<sub>2</sub> or in O<sub>2</sub> will normally yield two 511 keV photons ( $2m_e c^2$ ) in opposite directions. A germanium photon spectrometer nearby will record a 511 keV photopeak and also a Compton continuum at lower energies. The intrinsic

photopeak shape due to instrumental factors may be established with a monochromatic 514 keV gamma ray from the isotope  $^{85}\text{Sr}$ . Typically it has a full width at half maximum of just above 1.0 keV. It is generally found that the 511 keV annihilation line is broader, often about 2 keV. The extra broadening is a consequence of the resultant motion of the centre of mass of the  $e^+e^-$  pair. For example, with thermalized positron (0.025 eV) and a typical electron energy in a material of 6 eV, the photon energy may be Doppler shifted by 1 keV. Due to the isotropic emission from annihilating pairs, the photon energy in the direction of a fixed Ge detector will be spread about the peak position of 511 keV.

Although, by convolution analysis, it is possible to analyse a photopeak into three, four or five components (Rice-Evans *et al* 1992) corresponding to positrons annihilating with different groups of electrons, the purposes of this work are well served by using the conventional  $S$ -parameter to define changes in the height of the 511 keV line, normalized in area. This is customarily done by summing the contents of the central region of the line as recorded in a multichannel analyser, and dividing by the contents of the full line. In the present case the dispersion was 91 eV per channel, and  $S$  is defined as the contents of a central 17 channels, the full line being taken to be 91 channels.

Ps is the bound state of a positron with an electron. In the ground state it has a binding energy of 6.8 eV, half that of the analogous hydrogen atom. Ps exists as *ortho*-Ps (spins parallel) and *para*-Ps (spins opposed) with lifetimes of 147 ns and 125 ps respectively. As a result of spin conservation, *p*-Ps will decay via two 511 keV photons and *o*-Ps will decay via three photons sharing the total energy of 1.022 MeV. Under normal conditions statistics lead to a *p*-Ps/*o*-Ps formation ratio of  $\frac{1}{3}$ .

In contrast to positrons annihilating with electrons in a solid, free Ps has only a small motion of its centre of mass. This means there is only a small Doppler broadening, hence a narrower  $2\gamma$  line-shape; an increase in the proportion of positrons annihilating as *p*-Ps will cause a rise in the parameter  $S$ . Any rise in Ps formation is likely to result in more *o*-Ps, which may be recorded as more  $3\gamma$  decays. These add to the Compton continuum and hence changes in the amount of *o*-Ps may be recorded by the  $R$ -parameter, which is defined as the ratio of the analyser counts in the Compton region divided by the total counts in the whole spectrum.

### 3. Experimentation

Measurements have been made with a Ge detector of 1.1 keV resolution at 514 keV. Radioactive  $^{22}\text{NaCl}$  was deposited within a 3 mm diameter on 3  $\mu\text{m}$  aluminium leaf and composed in a sandwich. This positron source was packed in powder at the centre of an open thin-walled copper pot which was suspended within a sealed brass chamber lying in a Dewar of liquid nitrogen at 77 K. The sample temperature could be varied between 77 and 420 K. The  $\text{SiO}_2$  powder was Sigma S-5130 with a surface area of  $390 \text{ m}^2 \text{ g}^{-1}$ , a mean particle diameter of 70  $\text{\AA}$  and a density of  $0.13 \text{ g ml}^{-1}$ . The  $\text{Al}_2\text{O}_3$  powder was from BDH Chemicals, Pro 33138, mean particle diameter 150  $\text{\AA}$ . The procedure was to introduce a fixed quantity of gas, at a chosen initial starting pressure, prior to commencing a sequence of 1 h runs at prescribed temperatures. The pressure was monitored continuously with a Digiquartz gauge.

### 4. Results

Figure 1 shows the  $S$  parameter plotted as a function of temperature for  $\text{O}_2$  at various starting pressures on  $\text{SiO}_2$ . The vacuum run is seen to be low and nearly horizontal, indicating that

only a small amount of *p*-Ps is self-annihilating compared with the O<sub>2</sub> case. The curve is nearly flat, which reflects merely a small temperature dependence of the diffusion rate of Ps in SiO<sub>2</sub> (Chuang and Tao 1971). In contrast, the run at the highest pressure of O<sub>2</sub>, which was maintained for the whole run by maintaining a puddle of liquid O<sub>2</sub> at 77 K at the bottom of the brass chamber, shows a high initial *p*-Ps signal that begins to drop sharply with diminishing sample temperature below 200 K. Runs at intermediate pressures are also seen to decline but commencing at lower temperatures.

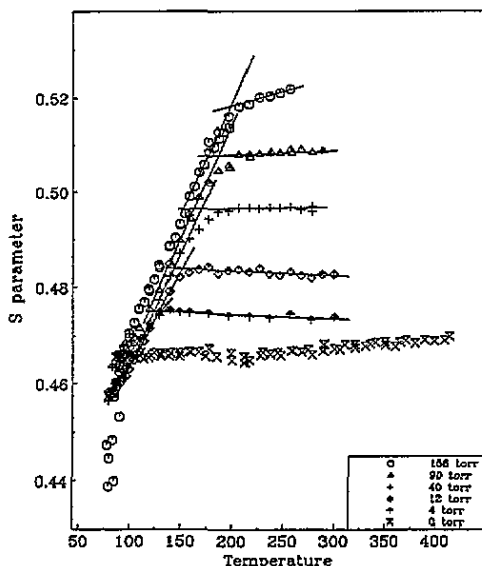


Figure 1. The parameter *S* (*p*-Ps) plotted against temperature for O<sub>2</sub> at various indicated starting pressures on SiO<sub>2</sub>. The straight-line fits are explained in the text.

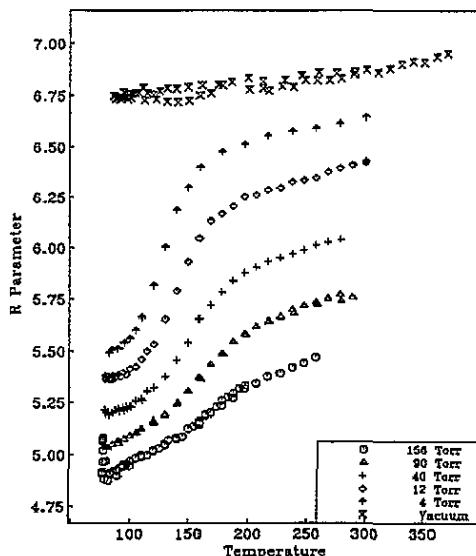


Figure 2. The parameter *R* (a measure of *o*-Ps) plotted against temperature for O<sub>2</sub> on SiO<sub>2</sub>.

Figure 2 shows the calculated *R* parameter for the same sets of data. For vacuum a high value indicates a large amount of *o*-Ps and the nearly flat curve suggests a temperature-independent emission rate for *o*-Ps from bare SiO<sub>2</sub> surfaces. The presence of O<sub>2</sub> reduces the amount of *o*-Ps, and so does diminishing temperature. Figures 3 and 4 show the equivalent curves corresponding to O<sub>2</sub> being condensed down on Al<sub>2</sub>O<sub>3</sub> powder. The features are very similar to those for SiO<sub>2</sub>.

## 5. Discussion

The curves are a result of Ps interactions in the O<sub>2</sub> gas and also of the physisorption of the O<sub>2</sub> as the temperature is reduced. The *S* parameter is highest for the greatest O<sub>2</sub> pressures, which reflects the well known fact that gaseous O<sub>2</sub> causes the conversion of *o*-Ps to *p*-Ps (Ferrell 1958). In the absence of O<sub>2</sub> the ratio *o*-Ps to *p*-Ps is expected to be 3/1, but increasing pressures of O<sub>2</sub> lead to reductions in the observed ratio.

The declines in both *S* and *R* are related to the condensation of O<sub>2</sub> on the substrates. A convolution analysis, not presented here, verified that these declines were accompanied by an increase in the free annihilation component. Initially, as the temperature is reduced a

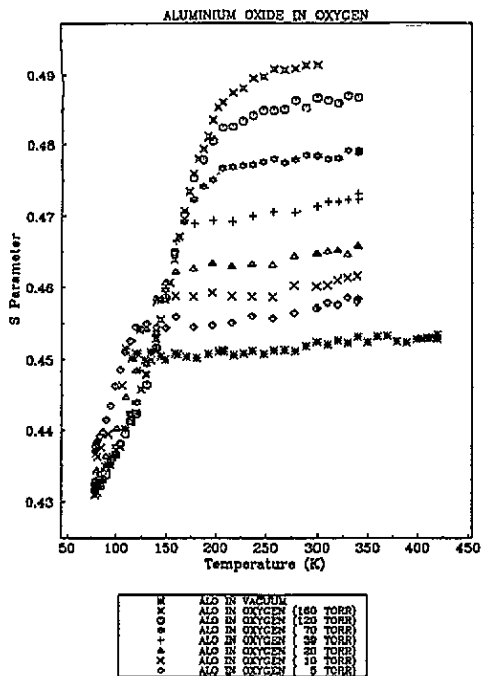


Figure 3. The parameter  $S$  against temperature for  $O_2$  on  $Al_2O_3$  powder.

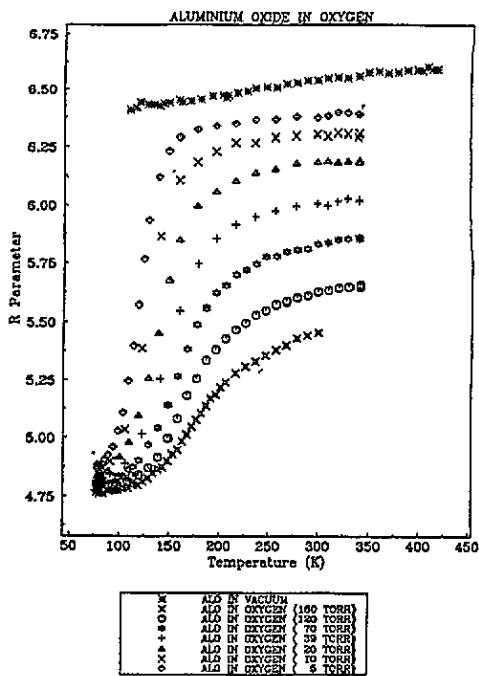


Figure 4. The parameter  $R$  against temperature for  $O_2$  on  $Al_2O_3$ .

monolayer will condense, with the equilibrium coverage being governed by the temperature. As temperatures are further reduced complete monolayer coverage is probable and then further layers will be adsorbed. For irregular powder surfaces it is to be expected that fixed-site physisorption will occur in which case the Langmuir model will apply (Dash 1975). This states the the relation between vapour pressure ( $P$ ) and  $x$ , the fractional monolayer coverage, is given by

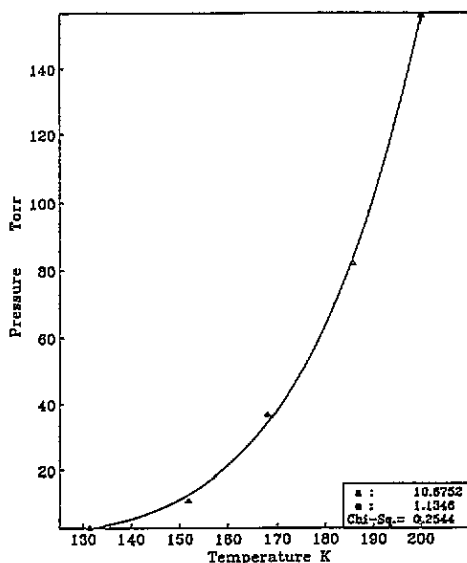
$$P = (2\pi m/h^2)^{3/2}(kT)^{3/2}[x/(1-x)]\exp(-\epsilon_0/kT)$$

where  $m$  is the mass of an oxygen molecule and  $\epsilon_0$  the binding energy governed by van der Waals forces. Although in the experiments  $x$  was not determined independently, the expression shows that it is sufficient to identify in a number of runs points of the same coverage, and then a plot of the vapour pressure against temperature will establish  $\epsilon_0$ .

In the data for  $S$  we have drawn computed straight lines through the high-temperature points, and also lines through the straight sections representing adsorption at the lower temperatures. We take the point of intersection to be a good indicator of the temperature of a certain value of  $x$ . Figure 1 shows the lines for  $O_2$  on  $SiO_2$ , and similar lines were drawn for  $Al_2O_3$ .

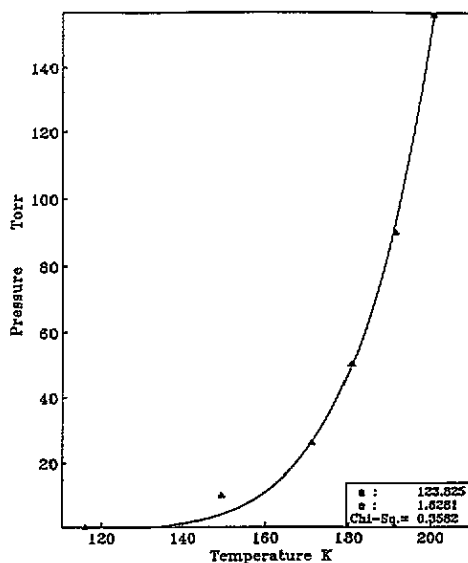
Figures 5 and 6 show the variation of the pressure with the intersection temperature for  $SiO_2$  and  $Al_2O_3$ , respectively. The Langmuir expression has been fitted to the points with a  $\chi^2$  minimization program and the best fits yielded values for  $\epsilon_0/k$  of  $1130 \pm 50$  K and  $1630 \pm 50$  K respectively. The former agrees well with the value of 1100 K found from isotherm measurements (Kiefl 1982, Brunauer *et al* 1938).

It is important to consider the action of the physisorbed  $O_2$  in suppressing the emission of Ps into the gas. One possibility is that it acts as a barrier that reflects the Ps back into



Langmuir fit to turning point on  $S$  parameter.  
unweighted fit

Figure 5. For O<sub>2</sub> on SiO<sub>2</sub>; the points indicate pressures corresponding to the intersection points of  $S$  (figure 1), with the line showing the best fit for the Langmuir model.



Langmuir fit to turning point on  $S$  parameter.  
unweighted fit

Figure 6. For O<sub>2</sub> on Al<sub>2</sub>O<sub>3</sub>; the points indicate the pressures corresponding to calculated intersection points for data in figure 3, with the Langmuir fit.

the SiO<sub>2</sub>—thus instead of a narrow Ps 511 keV component, the annihilation with normal SiO<sub>2</sub> electrons results in significant Doppler broadening and hence a smaller  $S$ . Similarly free  $o$ -Ps would be suppressed and  $R$  reduced. This would be in accord with the fact that the values for  $S$  at the lowest temperatures in the presence of O<sub>2</sub> fall below the vacuum value. However, reflection back into the grain appears unlikely for a combination of two reasons. First, it is known that SiO<sub>2</sub> has a negative work function (Sferlazzo *et al* 1987, Chang *et al* 1985). Second, although gaseous O<sub>2</sub> strongly converts  $o$ -Ps to  $p$ -Ps, it is known (Stewart *et al* 1990) from angular-correlation measurements with liquid O<sub>2</sub> that no narrow Ps component is seen in the 511 keV line, which implies that bubbles are not formed by Ps in bulk liquid O<sub>2</sub>, and hence that Ps is not repelled by O<sub>2</sub>. Ps may be formed in liquid O<sub>2</sub> (Stewart *et al* 1990) but it is quickly quenched and not observable.

The alternative explanation is that the Ps becomes trapped at the physisorbed layer, where it is chemically quenched. It has been suggested (Goldanskii *et al* 1975) that this might take place via the formation of an excited intermediate complex (PsO<sub>2</sub><sup>+</sup>), which, in the circumstances of site localization as in the fluid monolayer, would deactivate rapidly. This would lead to the Ps positron being picked off by an O<sub>2</sub> electron with anti-parallel spin, a consequent broadening of the photopeak, and a reduction in the parameter  $S$ .

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