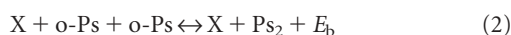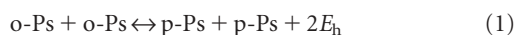# LETTERS

The production of molecular positronium

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It has been known for many years that an electron and its antiparticle, the positron, may together form a metastable hydrogen-like atom, known as positronium or Ps (ref. 1). In 1946, Wheeler speculated[2] that two Ps atoms may combine to form the di-positronium molecule (Ps$_2$), with a binding energy[3] of 0.4 eV. More recently, this molecule has been studied theoretically[4]; however, because Ps has a short lifetime and it is difficult to obtain low-energy positrons in large numbers, Ps$_2$ has not previously been observed unambiguously[5]. Here we show that when intense positron bursts are implanted into a thin film of porous silica, Ps$_2$ is created on the internal pore surfaces. We found that molecule formation occurs much more efficiently than the competing process of spin exchange quenching, which appears to be suppressed in the confined pore geometry. This result experimentally confirms the existence of the Ps$_2$ molecule and paves the way for further multi-positronium work. Using similar techniques, but with a more intense positron source, we expect to increase the Ps density to the point where many thousands of atoms interact and can undergo a phase transition to form a Bose–Einstein condensate[6]. As a purely leptonic, macroscopic quantum matter–antimatter system this would be of interest in its own right, but it would also represent a milestone on the path to produce an annihilation gamma-ray laser[7].

The use of positron traps and accumulators[8] has recently made it possible to perform experiments with systems containing more than one positron[5]. In particular, interactions between Ps atoms have been studied by implanting intense positron pulses into a thin film of porous silica. This material was chosen because Ps atoms are formed quite efficiently in it (and similar substances) after positron irradiation[9]. Ps can be formed in a long-lived triplet state known as ortho-positronium (o-Ps decays with a 142 ns vacuum lifetime into three gamma-ray photons) or a short-lived singlet state known as para-positronium (p-Ps decays with a 125 ps vacuum lifetime into two photons)[1]. Ps is formed in the bulk material where it generally has a short lifetime (<1 ns), but atoms that diffuse into internal voids may become trapped therein and live for an appreciable fraction of the vacuum lifetime[10]. Under these circumstances the Ps decay rate is usually determined primarily by pick-off annihilation[11] following interactions with the pore walls. If the Ps density is high enough, o-Ps atoms may interact with each other, which can lead to one of two distinct processes: spin exchange quenching (SEQ, equation (1))[12] or the formation of Ps$_2$ (equation (2)):

$$\text{o-Ps} + \text{o-Ps} \leftrightarrow \text{p-Ps} + \text{p-Ps} + 2E_h \qquad (1)$$

$$X + \text{o-Ps} + \text{o-Ps} \leftrightarrow X + \text{Ps}_2 + E_b \qquad (2)$$

Here E_h is the energy difference between the o-Ps and p-Ps ground states (that is, the hyperfine energy, which is ~1 meV)[1] and X represents a third body. For SEQ to occur the energy $2E_h$ must be transferred either to the outgoing p-Ps atoms or to the surrounding medium. For Ps$_2$ formation to occur a third body is always required to conserve momentum. Both of these processes may result in the

rapid annihilation of Ps and hence be detected via changes in Ps lifetime spectra. It is not, however, possible to distinguish between them using timing information alone.

The experimental arrangement was based on a Surko-type positron trap and accumulator[8] that has been described in detail elsewhere[13]. Positron pulses of about ten million particles with a sub-nanosecond time width were implanted into a 45% porous (porosity $P = 0.45$) silica film (made from tetraethoxysilane) that was 230 nm thick and had a 50-nm-thick non-porous capping layer[14]. The porous region contains interconnected pores with a diameter $d_{pore} \approx 4$ nm, and o-Ps that diffused into them had a lifetime of ~60 ns (ref. 10). With an incident beam areal density of 3×10^{10} cm^{-2} and a positronium fraction of ~10%, we estimate that the mean number of Ps atoms per pore was ~10^{-5} (assuming a uniform distribution throughout the entire thickness of the porous region). However, the positronium atoms have a long diffusion length (~1 μm) and visit ~10^4 pores on average during their lifetime, so that the overall probability of two atoms interacting is around 10%.

All positrons implanted into the sample eventually annihilate with an electron. Immediately following implantation, many positrons annihilate with electrons directly, without forming positronium, producing a large pulse of gamma rays. Gamma rays resulting from the annihilation of p-Ps atoms are often indistinguishable from the direct annihilation[15]. Because the triplet Ps decays much more slowly, its presence is indicated by gamma rays that arrive some time after the incident positron pulse. The annihilation radiation was detected by a PbF$_2$ Cherenkov radiator optically coupled to a fast photomultiplier tube (PMT). Lifetime spectra were obtained by directly measuring the PMT anode voltage $V(t)$ with a fast oscilloscope[16].

Density-dependent changes in the Ps decay rate were investigated by recording lifetime spectra at five different beam areal densities n_{2D}. When the beam density is increased, the Ps lifetime is reduced owing to interactions between Ps atoms (a process we refer to as 'quenching'). The spectra were analysed to determine the delayed Ps fraction f_d, defined as:

$$f_d = \int_{20\,\text{ns}}^{150\,\text{ns}} V(t)\mathrm{d}t \left/ \int_{-20\,\text{ns}}^{150\,\text{ns}} V(t)\mathrm{d}t \right. \qquad (3)$$

This parameter characterizes the amount of long-lived Ps present. For each group of five densities the mean value of f_d was calculated, and the deviation from that mean for each density, $\Delta f_d(n_{2D})$, was then used as a measure of the quenching. This procedure is equivalent to calculating the mean value of f_d at each density, but also takes into account the effects of small drifts that occur over the course of a run (typically ~12 h long). Figure 1 shows $\Delta f_d(n_{2D})$ for three representative temperatures; as in previous work, the expected linear density dependence of the quenching is observed[5].

The quenching signal would look the same whether it were due to Ps$_2$ formation or SEQ, because both of these mechanisms essentially convert long-lived triplet Ps into the short lived singlet state. We may, however, distinguish between the two mechanisms by considering the

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temperature dependence of the quenching. The basis for this differentiation is the fact that, neglecting three-body collisions, molecule formation is constrained to take place on a surface to conserve momentum, whereas SEQ is not. Ps may be thermally desorbed from surfaces, so we can control the fraction of atoms in the surface state via the temperature. This means that the temperature dependence of the quenching effect will be different for molecule formation and for SEQ; in the former case, heating will depopulate the surface states and therefore reduce the quenching, while in the latter case, heating would increase both the Ps density and the Ps–Ps interaction rate, which would increase the quenching. We observed that heating greatly reduces the quenching signal, unequivocally indicating molecule formation.

Figure 2a shows the temperature dependence of f_d. It is clear from the figure that the amount of long-lived Ps increases at higher temperatures, which we attribute to the thermal desorption of Ps from surface states. This leads to an increase in the amount of long-lived Ps present, because the lifetime of Ps on the surface is less than that in the voids. The data of Fig. 2a are divided into two distinct data sets; the difference between them is associated with the heating of the silica film to over 500 K for many hours (point 13). This was probably due to the thermal repair of positron trapping sites in the bulk material[17] or structural modifications caused by prolonged heating.

The solid lines in Fig. 2a are fits of an Arrhenius type, characteristic of thermally activated processes (see Methods). Such processes are typically parameterized by an activation energy E_a and a sticking (or accommodation) coefficient S, which is the probability that an atom remains on a surface immediately after impact. The thermal desorption of Ps from metallic surface states is well-known and has been extensively studied[18,19]. These activation energies are typically a few tenths of an electron volt and the sticking coefficients are close to unity, owing to the strong Coulomb interactions with the metallic electron gas[20]. There is also evidence to suggest that a Ps surface state exists on both crystalline[21,22] and amorphous SiO_2 (ref. 23) and our data are fully consistent with such a process. In this case S is very small because energy can only be exchanged with the surface by a weak coupling to phonons or other surface modes[24].

We quantify the quenching effect using the negative of the slope of $\Delta f_d(n_{2D})$, $Q \equiv -d\Delta f_d/dn_{2D}$. We used linear fits of $\Delta f_d(n_{2D})$, similar to those shown in Fig. 1, to all of the data to determine $Q(T)$, which is plotted in Fig. 2b. These data are separated into two distinct data sets in the same way as the data of Fig. 2a. The solid lines in Fig. 2b are fits similar to those of Fig. 2a (see Methods). Fitting the data in Fig. 2a yields activation energies (64 ± 23) and (83 ± 21) meV and sticking coefficients of $\log_{10}S = (-5.45 \pm 0.42)$ and (-5.34 ± 0.35) for the first and second data sets respectively. Similar fits were made to the data of Fig. 2b fixing the activation energy to be 74 meV, the average value obtained from the fits in Fig. 2a. The quality of the fits to all data sets reassures us that it is indeed appropriate to split the data into two sets, and that the model we use is essentially correct. The sticking
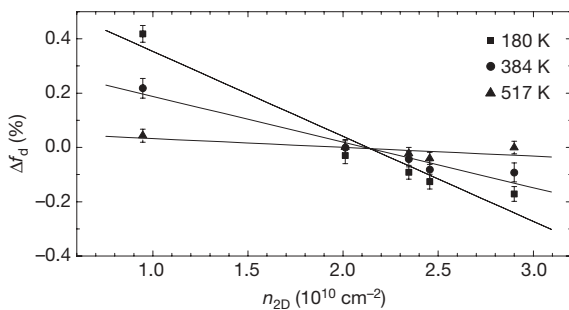
coefficients obtained in this way for the first and second runs were $\log_{10}S = (-5.12 \pm 0.12)$ and (-4.88 ± 0.12). The small sticking coefficient ($S \approx 10^{-5}$) is consistent with a very light particle of mass $2m_e$ (where m_e is the mass of the electron) that can only lose energy via phonons on a surface made of SiO_2 molecules (mass $\approx 1.1 \times 10^5 m_e$).

We obtain the same sticking coefficient (within errors) from all four data sets, which means that the data are consistent with a single thermally activated process, namely the thermal desorption of Ps. Moreover, $f_d(T)$ and $Q(T)$ are essentially mirror images of one another, indicating that these quantities depend oppositely on the relative population of the Ps surface state. This indicates that the quenching process must be taking place on the pore surfaces, and we conclude that it is the formation of positronium molecules.

There are some other possible mechanisms that could, in principle, give rise to the signal we observe. To be consistent with the data, any such mechanism must involve two or more positrons, take place on the internal pore surfaces and result in a reduction of the amount of long-lived Ps.

We can immediately rule out the thermal dissociation of Ps_2 molecules as the source of $Q(T)$, because this would be unlikely to follow the same temperature dependence as the thermal desorption. Also, the activation energy we measure (~ 0.074 eV) is much less than the ~ 0.4 eV Ps_2 binding energy[3]. Furthermore, half of the dissociated Ps atoms would be in a singlet state; these atoms would still contribute to the quenching signal and the maximum reduction in Q due to heating would therefore be 50%, which is not consistent with the data.

If the ''spur'' electrons[25] created in the silica by the incident positrons were able to interact with each other, it is possible that Ps formation could be inhibited in a manner that depends on the beam
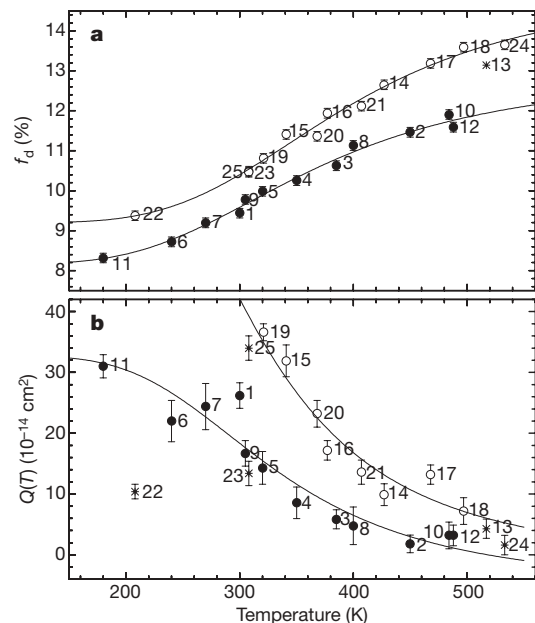
Figure 2 | Temperature dependence of f_d and Q. a, f_d as a function of temperature measured using a beam density of 0.9×10^{10} cm^{-2}. The 1σ error bars were determined by requiring the χ^2 value per degree of freedom for the fits to be close to unity. **b**, Q as a function of temperature obtained by fitting the density dependence of f_d. The 1σ error bars are from the fits used to obtain Q as in Fig. 1. The data points are labelled in the order in which they were taken. The lines are fits of equations (4) to the data. The filled and open circles are data from the first and second runs respectively, whereas the star symbols represent data ignored in the fits. Point 13 was apparently in transition between the low- and high-f_d runs. Points 22–25 were obtained using an improperly adjusted positron accumulator that yielded on average about twice as many positrons per pulse as the rest of the data. For these runs the beam intensity was unstable and actually of lower (and uncertain) areal density. These data yield reliable values for f_d, but we do not trust them to give usable measures of Q.

Figure 1 | Density dependence of the amount of long-lived Ps. The shift in f_d relative to the mean value for all beam densities is shown for three representative temperatures. The solid lines are linear fits used to determine the parameter Q as described in the text. The 1σ error bars are determined by the distribution of sets of at least 50 individual measurements each.

density. However, the spur electron cloud radius is around 10 nm, so this is extremely unlikely at the present beam densities, especially as only surface effects would be consistent with our observations.

If the Ps density were greatly enhanced on the surface relative to that in the pores, then the thermal desorption of Ps could lead to a reduction in Q even in the absence of Ps_2 molecule formation. For pore sizes of the order of the Ps thermal de Broglie wavelength we may describe the surface state Ps as the ground state of the cavity and the free Ps as the first excited state. We can then estimate the change in the mean Ps density that is due to desorption from the surface. For a reasonable approximation of the surface potential (4 atomic units wide, 1.8 eV deep[22]) and for a spherical cavity 4 nm in diameter we find that the surface density is actually less than the free Ps density by a factor of two. SEQ on the surface therefore cannot explain the temperature dependence of Q. Moreover, for a surface interaction where momentum is conserved, the Ps_2 formation rate compared to that for SEQ for a given density is highly favoured because the latter proceeds through a virtual Ps_2 state[26]. Thus, while there could be some SEQ between Ps atoms in the surface state, it is a second-order process and molecule formation is far more likely.

It is surprising that there is so little SEQ at higher temperatures. If we assume that there is no Ps_2 formation at all above 500 K, then the fits to the data of Fig. 2b imply that at room temperature Ps_2 formation is roughly ten times more likely than SEQ. This is consistent with SEQ being a second-order process, but one might expect that at higher temperatures when molecule formation is suppressed and the Ps density is increased SEQ would occur fairly efficiently. That it does not implies that spin exchanging collisions in the voids are suppressed.

Spin exchange from triplet to singlet Ps requires the transfer of the 1 meV triplet hyperfine energy to the kinetic energies of the final-state singlet Ps atoms (see equation (1)). Because the lowest energy surface and volume states are discrete (with energies of about 35 meV in a 4-nm-diameter pore), there are no nearby localized Ps states available to accommodate the extra energy. Thus, spin exchange will be highly suppressed not only in the volumes of a confined geometry, but also on the surfaces because it can only occur if accompanied by a phonon to conserve energy or by an improbable coupling to a chance pair of delocalized Ps states of the correct energy. This idea is supported by measurements made on a different sample[5] in which the pores were aligned to form long one-dimensional tubes; this type of pore geometry allows a continuous distribution of momentum in one dimension and would not be expected to suppress SEQ. With this sample we observed no thermal desorption of Ps, but a much stronger quenching signal, $Q = (154 \pm 5) \times 10^{-14}$ cm^2, that had no apparent temperature dependence. Further studies using samples of various geometries would help to elucidate the details of this process, but it is clear that in the disordered geometry of the porous silica film the observed quenching signal cannot be explained by SEQ.

The data presented here constitute evidence that we have observed molecular positronium. Our experiments suggest that a single-crystal quartz surface might be a good source of Ps_2 molecules, and work is underway to make a direct observation using a laser to excite a resonant molecular transition[27,28].

METHODS SUMMARY

We modelled the Ps thermal desorption assuming that Ps atoms are localized on the surfaces of single pores and that they can occupy one of M equivalent sites per unit area L^2. The yield as a function of temperature $Y(T)$ of Ps atoms annihilating in the voids depends on the ratio of the desorption rate to the total annihilation rate of the Ps on the surface. Following ref. 19 we write:

$$Y(T) = \left[1 + (4/e)(\lambda_{Ps}^2 M/L^2)S^{-1}(\gamma \lambda_{Ps}/\bar{v})\exp(E_a/kT)\right]^{-1} \quad (4)$$

where γ is the annihilation rate of Ps on the surface, the thermal de Broglie wavelength of a positronium atom is $\lambda_{Ps} = \sqrt{\pi \hbar^2/m_e kT}$, the thermal velocity $\bar{v} = \sqrt{4kT/\pi m_e}$, S is the Ps sticking coefficient[29] and E_a is the activation energy for thermal desorption of the bound Ps. We assume $M/L^2 = (\pi d_{pore}^2)^{-1} \approx 2 \times 10^{12}$ cm^{-2} and the surface state lifetime may be estimated from the ~3.5% overlap

of the Ps wavefunction with the SiO_2 surface[22]. Assuming the annihilation rate of Ps in the bulk material is 3 ns^{-1}, the surface state decay rate $\gamma \approx 10^8$ s^{-1}. Then we obtain:

$$Y(T) = \left[1 + (300\text{K}/T)^2 S^{-1}(7.2 \times 10^{-7})\exp(E_a/kT)\right]^{-1} \quad (5)$$

The solid lines in Fig. 2a and b are fits using the functions:

$$f_d(T) = f_0 + f_1 Y(T) \quad \text{and} \quad Q(T) = Q_0 + Q_1[1 - Y(T)] \quad (6)$$

respectively. The subscripts 0 and 1 refer to the non-thermal and thermal components (respectively) of f_d and Q.

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