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Evidence for positronium molecule formation at a metal surface

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We have observed a reduction in the amount of positronium emitted from an atomically clean Al(111) surface that depends on the incident positron beam density. We interpret this as evidence for the formation of molecular positronium, created following interactions between two pseudopositronium atoms trapped in a surface state. We find that this process is highly sensitive to the condition of the surface and is easily suppressed by changes thereupon. The implications of our data for planned spectroscopic studies of molecular positronium are discussed, as well as improvements to the experimental procedure that will allow more detailed measurements of the thermodynamics of the formation of this molecule from metal surfaces.

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I. INTRODUCTION

It has recently been shown that the positronium molecule (Ps_2) may be formed following interactions between positronium (Ps) atoms on the internal surfaces of porous silica films [1]. These surfaces, however, are not well defined, and any analysis applied to them must therefore be approximate. Moreover, attempts to measure the properties of such Ps_2 via laser spectroscopy may be complicated by the fact that the molecules are confined in pores. Thus, it is desirable to produce Ps_2 that is emitted into vacuum from a well characterized surface, allowing for more precise measurements. One way to achieve this is by creating a high density of positrons or positronium atoms on the surface of a single crystal metal such as Al [2] or an insulator such as quartz [3,4].

It is well known that Ps may be created when low energy positrons are implanted into a variety of metals [5]. If the subsequent diffusion length in the metal is longer than the implantation depth such positrons may return to the surface where they may be re-emitted into the vacuum [6], become trapped in a surface state [7], or capture an electron and be emitted as Ps atoms [8]. For metals a positronium "work function" does not have a precise meaning without further definition since the atom does not exist inside the bulk material. However, one may define a positronium work function in terms of the maximum kinetic energy of Ps formed directly from thermalized positrons in the bulk solid during positron emission as $\phi_{Ps}=\phi_+ + \phi_- - \frac{1}{2}R_\infty$, where ϕ_+ and ϕ_- refer to the positron and electron work functions, respectively, and $\frac{1}{2}R_\infty=6.8$ eV is the (ground state) Ps binding energy [9,10]. Ps may also be formed from positrons originally trapped in a surface state; these positrons are strongly correlated with surface electrons and may be regarded as pseudo-Ps atoms [11]. In this case the minimum energy needed to cause emission of a positronium atom into the vacuum is the surface activation energy $E_a=E_s+\phi_- - \frac{1}{2}R_\infty$, where E_s is the binding energy of the positron in the surface state. The thermal desorption rate of such positronium is given by an analogue to the Richardson-Dushman equation [12–14]

$$\Gamma_{\mathrm{Ps}} = S_{\mathrm{Ps}} \frac{kT}{h} \exp(-E_a/kT). \tag{1}$$

Here S_{Ps} is the Ps surface sticking coefficient [15], T is the sample temperature, k is Boltzmann's constant, and h is Planck's constant. If the density of surface state positrons is high enough, it is possible for the dipositronium molecule Ps_2 to be formed. This molecule has a binding energy of $E_b \sim 0.44$ eV [16]. The Ps_2 emission rate is given by [2]

$$\Gamma_{\mathrm{Ps}_2} = S_{\mathrm{Ps}_2} \frac{\hbar m_e n_+}{m_+^2} \exp\{-(2E_a - E_b)/kT\}. \tag{2}$$

Here S_{Ps_2} is the Ps_2 sticking coefficient, m_+ refers to the effective positron mass on the surface, m_e is the free electron mass, and n_+ is the positron surface density. Since E_a is ~ 0.34 eV for Al(111) [17], Ps_2 emission could occur at rates comparable to those for Ps emission. For example, if Ps_2 is formed at room temperature we should expect for $n_+=1\times10^{10}$ cm^{-2}, corresponding to the highest surface positron densities obtained in this work, spontaneous Ps_2 emission to occur at about 10% of the rate for Ps emission (assuming that m_+/m_e and $S_{\mathrm{Ps}}/S_{\mathrm{Ps}_2}$ are both close to unity) [2].

If dipositronium is created, then some Ps that might otherwise have been thermally desorbed in the long lived triplet state instead decays at the Ps_2 rate of ~ 4 ns^{-1} [18]. This means that an experimental signal of Ps_2 formation is a reduction in the amount of long lived Ps present. Since the molecule decays predominantly via two gamma rays while the long-lived triplet Ps decays via three photons one could, in principle, detect Ps_2 using energy selective detectors [19]. For simplicity we have used single-shot lifetime measurements [20] to determine the fraction of positrons decaying as long-lived positronium.

II. EXPERIMENTAL PROCEEDURE

The experiments were carried out using a positron accumulator that has been described elsewhere [21]. A two stage Surko trap [22] was used to supply positrons to an accumulator, which can store plasmas containing up to 1×10^8 particles. These plasmas are then ejected by a 300 V pulsed harmonic potential, which compresses them to a time width

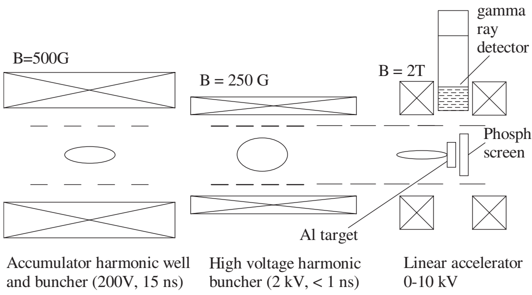

FIG. 1. Layout of the positron accumulator, harmonic bunchers, and magnetic fields. The 2 T pulsed magnetic field compresses the plasma to a full width at half maximum of around 200 microns. The sample preparation chamber (not shown) is adjacent to the high field target chamber. A long travel manipulator allows the sample to be retracted into an independent vacuum system with a base pressure below 1×10^{-10} Torr where the sample is cleaned and annealed, and where the surface is characterized via Auger electron spectroscopy.

of ~15 ns, following which a higher voltage (2 kV) harmonic buncher compresses the plasma to a sub ns pulse [23]. The plasma is also compressed spatially in the accumulator by a “rotating wall” electric field [24] to a FWHM of ~1 mm. The layout of the accumulator, harmonic bunchers and target region are shown in Fig. 1. The parameters quoted refer to pulses containing $\sim1.5\times10^7$ positrons, which were of sufficiently low intensity to avoid detector saturation.

A pulsed magnetic field of ~2 T at the target further compresses the beam to 200 μm (FWHM). The size of the beam on target may be varied without changing the magnetic field by allowing the fully compressed plasma to expand before ejection. This is achieved by turning off the rotating wall electric field for periods of up to 3 s. It is desirable to keep the magnetic field at the target constant since it is sufficiently strong to quench positronium by mixing the $m=0$ substates [25]. As well as this, varying the magnetic field could also affect the beam transport and the operation of the detectors.

In this way sub-ns positron pulses of varying areal density n_{2D} were delivered to the target region about once per minute. The target used was an Al (111) single crystal oriented to within 0.5° of the stated orientation and polished to a mirror finish. Prior to data collection the sample was cleaned by bombardment with 800 eV Ar^+ ions, annealed (at 600 °C) and the surface contamination measured using Auger electron spectroscopy. The primary contaminants observed were oxygen and carbon, both of which typically had less than 2% of a monolayer coverage following cleaning.

Following positron implantation into the sample single shot lifetime spectra were recorded [20]. The detector used was a PWO_4 crystal attached to an XP2020 photomultiplier. This arrangement had a time response of ~15 ns (FWHM), determined primarily by the decay time of the scintillator [26]. The lifetime spectra were automatically integrated to determine the parameter f_d, defined as the sum of the counts in the region from 20 to 150 ns divided by the counts in the region from −20 to 150 ns; this number is a measure of the Ps fraction (that is, the fraction of incident positrons that form Ps) and is reduced if Ps_2 is formed.

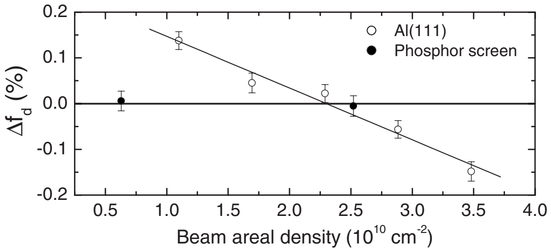

FIG. 2. An example of the change in f_d relative to the group mean (see text) as a function of the beam areal density using a clean Al(111) sample at room temperature. The solid line is a linear fit to the data whose slope yields the quenching parameter Q; in this case, $Q=(-11.9\pm1.1)\times10^{-14}$ cm^2. Also shown are two points taken using a phosphor screen biased to −5 kV instead of the Al sample. In this case Q is consistent with zero, in agreement with the expectation that little or no Ps (and therefore Ps_2) should form under these circumstances.

In order to minimize the effects of small drifts that may occur over the course of a long run the data were recorded in groups of five consecutive pulses taken at five different densities: for each group the mean value of f_d was calculated, and then the difference from the mean for each density Δf_d was determined. That is,

$$\Delta f_d(n_{2D}) = f_d(n_{2D}) - \frac{1}{m}\sum_{1}^{m} f_d(n_{2D}) \quad (3)$$

with $m=5$. Figure 2 shows Δf_d as a function of the incident beam density. Each datum is the mean of approximately 100 shots. The quenching signal is defined by the parameter $Q = d\Delta f_d/dn_{2D}$, which is obtained from a linear fit as shown in the figure.

III. RESULTS

The linear dependence of Δf_d on the beam density as observed in Fig. 2 is just what would be expected for Ps_2 formation, and is similar to the signal observed using porous silica [1] (although the magnitude of the signal here is significantly smaller). In that work the quenching signal was not in itself evidence for Ps_2 formation since the interaction of two Ps atoms can lead to spin exchange quenching (SEQ), which has an identical signal [27]. In this case, however, the metallic surface state “pseudo-Ps” [11,28] is not in a well defined spin state, and SEQ cannot occur. In addition, any Ps atoms that have left the surface will have little chance of interacting with other Ps atoms due to their comparatively low density in vacuum ($\sim10^{12}$ cm^{-3}). Thus, the data of Fig. 2 may be attributed to the formation of molecular positronium at the surface of a clean Al(111) single crystal surface.

Having obtained evidence for Ps_2 formation on a metal surface it had been our intention to carefully measure this process as a function of temperature, from which data we expected to obtain an experimental verification of the Ps_2 binding energy [2]. Unfortunately we were not able to do so because the long run times required meant that sample contamination was a serious problem. Figure 3 shows the de-

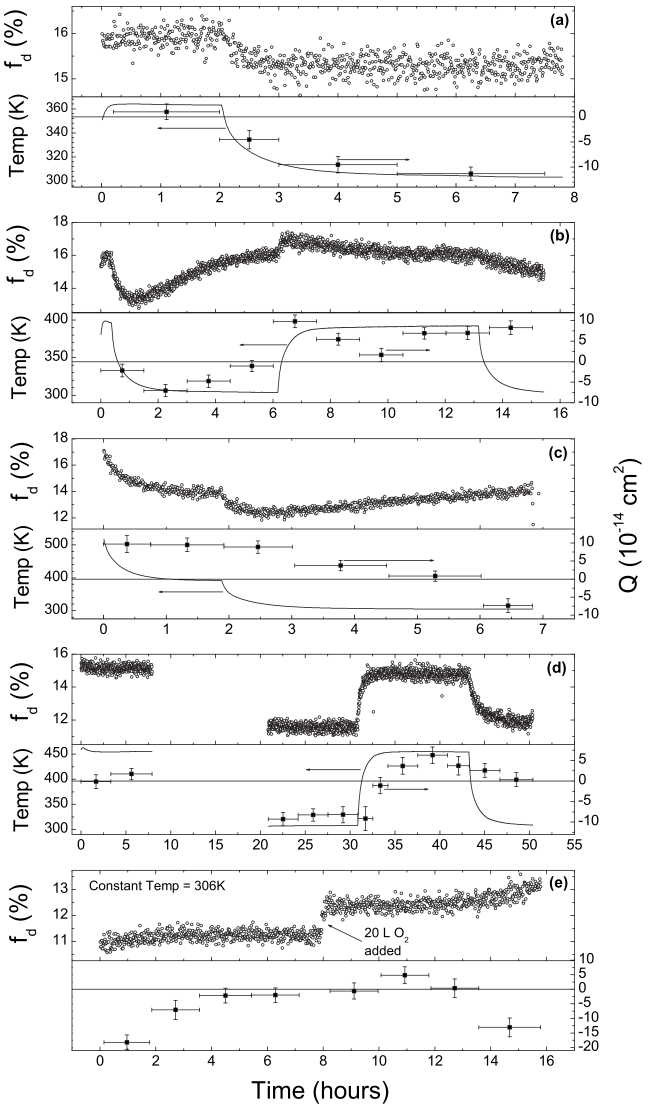

FIG. 3. The delayed fraction, quenching signal and sample temperature as a function of time for five separate runs. The horizontal error bars indicate the run time over which Q has been averaged. The sample is clean at the beginning of each run. The gap in run (d) is due to the loss of the positron beam, as described in the text. Run (e) was performed at a constant temperature of 306 K, and 20 Langmuir (1 Langmuir$=10^{-6}$ Torr exposure for 1 s.) of oxygen was deliberately introduced after around 8 h.

layed positronium fraction, the quenching signal, and sample temperature as a function of time for five separate runs. In all cases the sample was cleaned before the start of the run. It is clear from the data that the reproducibility was poor, although it is not clear exactly why. The one consistent effect observed was that a clean sample at room temperature provided a quenching signal that is consistent with the formation of Ps_2 molecules with an average quenching signal $Q=-(9.9\pm2.7)\times10^{-14}\ \mathrm{cm}^2$. This average signal implies $\Delta f_d=Qn_{2D}=0.35\%$ compared to an average room temperature thermal Ps contribution to the delayed fraction $f_d^{\mathrm{th}}\approx5\%$. This is in reasonable agreement with the prediction arrived at above using Eqs. (1) and (2) [29].

Figure 3(a) shows the quenching signal Q appear as the sample is cooled. This is qualitatively consistent with a model in which the thermal desorption of Ps atoms is in competition with the formation of Ps_2 molecules, although the small temperature variation implies that the actual situation may be more complicated. A similar effect is observed in Fig. 3(b); however, in this case we see that Q deteriorates after a few hours, and then becomes positive. Moreover, when the sample is cooled again there is no quenching effect observed. In Fig. 3(a) the delayed positron fraction f_d varies in lockstep with the temperature, as we would expect (at least over the small range of variation here). In Fig. 3(b), however, while this is initially the case, after around an hour f_d begins to climb while the temperature remains fixed. (This is typical of sample contamination, which is not necessarily deleterious to the emission of thermal Ps. For example, even low levels of O_2 coverage can reduce the Ps activation energy and increase the amount of thermal desorption [30,31]). In Fig. 3(c) we see just the opposite; after the sample has cooled, the delayed fraction slowly climbs up to around 15% whereupon the quenching signal grows stronger, apparently under conditions similar to those seen in Fig. 3(a). In Figs. 3(b)–3(d) positive values of Q are observed, indicating that the amount of Ps emitted increases when the positron beam density is increased. This effect was consistently observed and appears to be related to contamination.

Figure 3(d) shows a run in which there is a gap of ~13 h. This occurred because a malfunction in the helium expander caused the neon moderator [32] to be lost, which essentially turned off the positron beam without changing any other experimental parameters. When the beam was restored the sample had been exposed to normal operational vacuum conditions for ~20 h. The quenching signal then looked very similar to those obtained when a clean sample is inserted. Subsequent heating of the sample then led to a loss of the quenching signal, and we again observed positive Q values after about 5 h. Moreover, cooling the sample again did not lead to a restoration of the quenching signal, even though the Ps fraction returned to a similar level.

Figure 3(e) shows a run taken at a constant temperature, with O_2 added to the sample after about 8 h. Here the quenching signal disappears during the course of the run and is unaffected by the addition of the gas. The fact that f_{d} hardly changes while the quenching signal disappears during the first 8 h implies that f_{d} is not in itself a good indicator of the amount of the surface contamination that is detrimental to Ps_2 formation. The Ps fraction does increase when the oxygen is added, but since there is no quenching signal to suppress, Q is unaffected. We note that the additional oxygen did not lead to a positive Q signal. About 5 h after adding O_2 the Ps fraction begins to climb again, and a quenching signal appears, apparently due to the addition of yet more contamination on top of the oxygen layers applied. Clearly, there are complicated surface mechanisms at play.

IV. DISCUSSION

We do not yet fully understand the reasons for the positive Q values observed in Figs. 3(b)–3(d), which indicate an increase in the delayed Ps fraction when the positron beam density is increased. This effect is the opposite of what we expect for the dipositronium signal. We speculate that if Ps_2 formation is reduced by contamination then some other effects which increase the Ps thermal desorption rate at higher beam densities may become apparent. These could be localized heating, small variations in the surface dipole potential, or a positron Fermi energy induced by the presence of many positrons at the surface, and therefore dependent on the beam density. We estimate the magnitude of these effects assuming a pulse of 1.5×10^7 positrons with a mean energy of 1.5 keV and a full width at half maximum of 200 μm that is implanted to a mean depth 25 nm [33].

The maximum beam induced local sample temperature increase is less than 0.5 K [34], from which we would expect an increase in the positronium fraction of less than 0.01% [35]. This is far too small to explain the observed data.

On the other hand, the change in the surface dipole potential and positron Fermi energy due to the positron surface density could change the positronium fraction significantly. A sheet of 10^{10} positrons per cm^2 represents a charge density ρ_s of approximately $1.6\times 10^{-9}\ \mathrm{C/cm}^2$. If we approximate this as an infinite, uniform sheet of charge, we should expect it to generate an electric field $E=\rho_s/\varepsilon_0\sim 18\ \mathrm{keV/cm}$, where ε_0 is the permittivity of free space. If the surface positron arrangement corresponds to that of pseudo-Ps atoms [11], an average distance of order $\delta\approx\sqrt{27.2\ \mathrm{eV}/E_a a_B}\approx 0.5$ nm above the surface, we then have a change in the surface dipole potential $\Delta\phi=\kappa E\delta\approx\kappa\times 1$ mV, where a_B is the Bohr radius and $\kappa<1$ is a factor that depends on the details of the charge rearrangement and of the shape of the surface potential well [36]. The sign of the change in the surface dipole is such as to decrease the electron work function, and lower E_a. We assume that the activation energy changes by an amount $\Delta E_a=\kappa' e\Delta\phi$ where $\kappa'<1$ is another factor depending on the details of the charge distribution on the surface. For $\kappa\kappa'\approx 0.1$ the change of the thermal Ps emission rate at room temperature leads to a fractional increase in the delayed fraction $\sim 1\ \mathrm{meV}/25\ \mathrm{meV}=4\times 10^{-3}$. From this, and for $f_\mathrm{d}=0.15$, we should expect a quenching signal of $Q=f_\mathrm{d}\times(4\times 10^{-3}/2.4\times 10^{10})\approx 2\times 10^{-14}$, which is of the same order of magnitude as the positive Q values observed. That $\kappa\kappa'$ could be rather small is gleaned from our experience with the effect of putting a fraction of a monolayer of Cs on a clean Si surface [17]. Whereas in that work it was expected (with the tacit assumption $\kappa\kappa'=1$) that total spontaneous desorption of the surface Ps on Si(100) would occur with only a 0.2 eV change in the electron work function, a half monolayer of Cs was required, which probably changed the work function by about 2 eV. It is likely that $\kappa\kappa'$ varies greatly with surface conditions, and our crude estimate clearly does not address any of the subtleties associated with this mechanism; it does, however, support the idea that it is a possible explanation for the positive Q values.

The presence of positrons on the Al crystal surface may also lower the activation energy for Ps thermal desorption by an amount equal to the surface positron Fermi energy E_F. Assuming two degenerate bands of free particles of effective mass equal to the free electron mass, the positron Fermi energy is $E_F=\pi\hbar^2 n_{2\mathrm{D}}/m_e=0.024\ \mathrm{meV}\times(n_{2\mathrm{D}}/10^{10}\ \mathrm{cm}^{-2})$. Including corrections for interaction effects could increase this figure by a factor comparable to the Wigner-Seitz radius $r_s\approx 10$ (in atomic units) leading to effects of the same size as expected for the dipole layer change discussed in the previous paragraph [37].

We conclude that, whereas thermal effects associated with the dense positron beam probably have little influence on our Ps_2 signal, the surface positron Fermi energy and surface dipole energies could cause significant changes in Q that depend on the detailed properties of the sample surface. Our estimates of the extent to which these mechanisms may contribute to the quenching signal are crude, however, and further experimental and theoretical work is required to understand this effect fully.

The data of Figs. 3(d) and 3(e) could indicate that radiation effects associated with the positron beam itself have an effect on the sample surface. This could be caused by the ionization of residual gas atoms in the vicinity of the buncher by the ∼200 eV positrons (emitted from the accumulator), which would then be accelerated by the 2 kV harmonic buncher potential. This would effectively ion bombard the sample during the course of a run, but only if the positrons were present.

Another possibility is that a chemical change occurs on the sample surface due to incident positrons ionizing adatoms already present. Following a long exposure to the residual gases of the vacuum, a contaminant layer may build up on the initially clean Al(111) surface. This layer could conceivably be modified by repeated positron bombardment. Since the sample is held in a fixed location relative to the center of the positron beam, this might cause a measurable change in f_d as a function of beam density associated with the changing average chemical condition of the surface. For the recently cleaned Al(111) surface we do not think this is a likely possibility. However, after several hours of exposure to the positron beam, we have observed changes in Q that could be explained by an effect of this kind, for example, the fact that Q in Fig. 3(d) is present after the sample has been exposed to the usual residual gases in the sample chamber with the positron beam off.

We note that Auger spectra taken after long runs did not show any signs of surface contamination from the SF_6 cooling gas. However, if these molecules had a short surface residence time, then it could be possible for them to affect the measurements without ever being visible in post-run scans. To test this hypothesis, Auger spectra were recorded on a clean Al(111) sample at room temperature. Before exposure to SF_6, the peak-to-peak amplitude at 152 eV (corresponding to S) divided by the peak-to-peak amplitude at 66 eV (corresponding to Al) was $V_\mathrm{S}/V_\mathrm{Al}=(-0.55\pm 0.22)\%$ determined by a least squares fit to the derivative of a Gaussian line shape constrained to have the expected width and location of the S peak. We estimate that $V_\mathrm{S}/V_\mathrm{Al}=2\%$ would correspond to ∼1% of a monolayer of S on Al. Next, SF_6 gas was admitted into the chamber at a pressure of $\sim 1\times 10^8$ Torr (approximately ten times higher than the SF_6 pressure in the target chamber during a run) while recording Auger spectra. In nine scans taken at intervals of 90 s an average $V_\mathrm{S}/V_\mathrm{Al}=(0.84\pm 0.08)\%$ was found by using an unconstrained derivative of a Gaussian fit. In the next nine scans we found $V_S/V_{Al} = (1.05 \pm 0.13)\%$. Scans taken at various gas exposures about 90 s after turning off the gas showed no such contamination, from which we deduce that either the gas has a short residence time or that surface contamination only occurs when the gas is ionized (in this case by the incident electron beam instead of positrons). We conclude that a contamination effect could possibly be associated with the disappearance of our Ps_2 signal, but that this explanation would imply a remarkably high sensitivity to contamination at levels below about 0.1% of a monolayer.

V. CONCLUSION

While there is certainly good reason to expect that Ps_2 formation would be affected by the sample temperature [2], the present data cannot be interpreted in this way due to the low precision, poor reproducibility, and ill defined mechanisms giving rise to positive Q values, as well as possible beam dependent processes that affect the state of the sample. The only reliable data appear to be those obtained at room temperature relatively soon after cleaning. We have to conclude that, while it is very likely that Ps_2 formation on a metal surface has been observed, a detailed measurement of the temperature dependence of this process is beyond the capability of the present experimental arrangement.

The main difficulty with the current effort is the small Ps_2 signal. This is in part due to the short lifetime of the positron surface state [$\sim$0.5 ns [38]]. Since the beam pulse is typically (0.9 ± 0.1) ns wide, not all of the available positrons are being utilized at once, and the time needed to acquire data of sufficient statistical precision is incompatible with the vacuum conditions. Obviously, improving the vacuum would mitigate this problem, but without knowing exactly what surface effects are important it is also desirable to increase the Ps_2 signal as much as possible.

It is not known if ions created by the positron beam actually do affect the sample in any way. Although the base pressure in the target chamber is low ($<5 \times 10^{-11}$ Torr), it rises to $\sim 1 \times 10^{-9}$ Torr when the accumulator is operational due to leakage of the nitrogen buffer gas and SF_6 cooling gas used in the trap and accumulator [21]. We note that in general no evidence for these gases was observed on the sample surface by Auger analysis after a run. Since we did not observe precisely the same spot that had been bombarded with positrons, and since that spot was probably much smaller than the Auger spectrometer electron beam diameter, we would not expect to see evidence of beam induced chemical effects. Furthermore, since we had no way to monitor the surface roughness, we do not know if it was affected either. Visual inspection of the sample following 100 hours of ion bombardment clearly shows degradation from the initially perfect mirror finish of the surface in the form of apparently rough, dull patches. In future experiments such contamination as does occur will be significantly reduced by introducing a differential pumping section between the accumulator and the buncher and target chamber.

There is another potential problem that can be caused by the buncher. If variations in the space charge potential of the positron plasma (caused by changing the beam density) change the transfer time from the accumulator to the high voltage buncher, then the mean beam energy may also change. Since the Ps fraction is sensitive to the beam energy [35], a density-dependent beam energy could disguise (or exaggerate) a Ps_2 signal. This was monitored by recording the time of flight of the beam (that is, the interval between the accumulator dump signal and the prompt annihilation peak). Any data for which there was a correlation between the beam density and the time of flight were discarded. This problem will be entirely eliminated in the next system upgrade in which the pulsed beam will be remoderated [39] by implantation into a thin Ni foil [40]. This will substantially increase the beam density, and the resulting pulse will be almost monoenergetic.

Auger analysis on the sample after a run quite often (but not always) showed no significant contamination, even if the initial Ps_2 signal had disappeared. The presence of hydrogen on the Al surface could, in principle, influence Ps_2 formation by changing the activation energy E_a. Neither surface hydrogen nor variations in roughness would be detected by Auger analysis [41]. In addition, the Auger analysis would be insensitive to the 0.25 mm diameter area being irradiated by the high density positron beam if that is a factor affecting the surface quality.

Increasing the positron beam density by at least an order of magnitude might allow us to investigate the effects of contamination more thoroughly by permitting data to be accumulated faster than the contamination. Indeed, with such a beam the process of Ps_2 formation could, in principle, become an extremely sensitive surface probe that may provide a unique diagnostic capability.

To summarize, we have observed evidence for the formation of molecular positronium on a metal surface, but our present experimental capabilities are unable to provide any detailed information regarding the thermodynamics of this process. We believe that this may be rectified by remoderating the positron beam so that the density and the Ps_2 signal are both increased. This will also help to ensure that the beam is fully monoenergetic and the vacuum conditions are improved; work is underway to realize these conditions. With a suitably modified apparatus we hope also to understand a number of intriguing aspects of our present measurements, such as the effect of the beam on the sample surface and the positive Q measurements. That Ps_2 formation appears to occur on a metal surface at all is encouraging, as it promises a copious source of such molecules in vacuum, which will facilitate laser spectroscopy of its excited molecular states [42].

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[1] D. B. Cassidy and A. P. Mills, Jr., Nature (London) **449**, 195 (2007).

[2] A. P. Mills, Jr., Nucl. Instrum. Methods Phys. Res. B **192**, 107 (2002).

[3] A. P. Mills, Jr., Appl. Surf. Sci. (to be published).

[4] R. Saniz, B. Barbiellini, P. M. Platzman, and A. J. Freeman, Phys. Rev. Lett. **99**, 096101 (2007).

[5] P. J. Schultz and K. G. Lynn, Rev. Mod. Phys. **60**, 701 (1988).

[6] Positron reemission is only possible if the material in question has a negative positron work function or the emitted positrons are not fully thermalized. A. P. Mills, Jr., P. M. Platzman, and B. L. Brown, Phys. Rev. Lett. **41**, 1076 (1978).

[7] C. H. Hodges and M. J. Stott, Solid State Commun. **12**, 1153 (1973).

[8] K. F. Canter, A. P. Mills, Jr., and S. Berko, Phys. Rev. Lett. **33**, 7 (1974).

[9] See for example A. P. Mills, Jr., in *Positron Spectroscopy of Solids*, edited by A. Dupasquier and A. P. Mills, Jr. (IOS Press, Amsterdam, 1995), pp. 209–258.

[10] The neutral work function $\phi_{Ps}=\phi_{+}+\phi_{-}$ has been introduced by D. W. Gidley and W. E. Frieze, Phys. Rev. Lett. **60**, 1193 (1988).

[11] P. M. Platzman and N. Tzoar, Phys. Rev. B **33**, 5900 (1986).

[12] J. B. Pendry, J. Phys. C **13**, 1159 (1980).

[13] S. Chu, A. P. Mills, Jr., and C. A. Murray, Phys. Rev. B **23**, 2060 (1981).

[14] A. P. Mills, Jr. and L. Pfeiffer, Phys. Rev. B **32**, 53 (1985).

[15] A. P. Mills, Jr., E. D. Shaw, M. Leventhal, P. M. Platzman, R. J. Chichester, D. M. Zuckerman, T. Martin, R. Bruinsma, and R. R. Lee, Phys. Rev. Lett. **66**, 735 (1991).

[16] J. Usukura, K. Varga, and Y. Suzuki, Phys. Rev. A **58**, 1918 (1998).

[17] A. P. Mills, Jr., Solid State Commun. **31**, 623 (1979).

[18] E.g., D. M. Schrader, Phys. Rev. Lett. **92**, 043401 (2004); S. Bubin and L. Adamowicz, Phys. Rev. A **74**, 052502 (2006).

[19] The positronium fraction could be obtained from a burst of millions of gamma rays via the instantaneous $3\gamma/2\gamma$ ratio, measured using the anode signals from a pair of fast detectors, one of which responds to all the photons equally while the other is partially shielded from the lower energy 3γ-decay events by a few mm of lead.

[20] D. B. Cassidy, S. H. M. Deng, H. K. M. Tanaka, and A. P. Mills, Jr., Appl. Phys. Lett. **88**, 194105 (2006).

[21] D. B. Cassidy, S. H. M. Deng, R. G. Greaves, and A P Mills, Jr., Rev. Sci. Instrum. **77**, 073106 (2006).

[22] C. M. Surko and R. G. Greaves, Phys. Plasmas **11**, 2333 (2004).

[23] A. P. Mills, Jr., Appl. Phys. (Berlin) **22**, 273 (1980).

[24] F. Anderegg, E. M. Hollmann, and C. F. Driscoll, Phys. Rev. Lett. **81**, 4875 (1998); R. G. Greaves and C. M. Surko, *ibid.* **85**, 1883 (2000).

[25] A. Rich, Rev. Mod. Phys. **53**, 127 (1981).

[26] D. B. Cassidy and A. P. Mills, Jr., Nucl. Instrum. Methods Phys. Res. A **580**, 1338 (2007).

[27] D. B. Cassidy, S. H. M. Deng, R. G. Greaves, T. Maruo, N. Nishiyama, J. B. Snyder, H. K. M. Tanaka, and A. P. Mills, Jr., Phys. Rev. Lett. **95**, 195006 (2005).

[28] K. G. Lynn, A. P. Mills, R. N. West, S. Berko, K. F. Canter, and L. O. Roellig, Phys. Rev. Lett. **54**, 1702 (1985).

[29] We note that previously the thermal Ps fraction was observed to be very small at room temperature [17], whereas in the present study the thermal Ps fraction at room temperature was almost always about 1/3 of the maximum possible. This presumably indicates a difference in the surface conditions of the two samples.

[30] K. G. Lynn, Phys. Rev. Lett. **44**, 1330 (1980).

[31] A. P. Mills, Jr., E. D. Shaw, M. Leventhal, R. J. Chichester, and D. M. Zuckerman, Phys. Rev. B **44**, 5791 (1991).

[32] A. P. Mills, Jr and E. M. Gullikson, Appl. Phys. Lett. **49**, 1121 (1986).

[33] A. P. Mills, Jr. and R. J. Wilson, Phys. Rev. A **26**, 490 (1982).

[34] The total energy deposited by a fully compressed positron pulse is $U=1.5\times10^{7}\times1500\ \mathrm{eV}\times1.6\times10^{-19}\ \mathrm{J/eV}=3.6\times10^{-9}$ J. The total volume into which this energy is deposited is $V=\pi\times(0.02)^{2}\times2.5\times10^{-6}\ \mathrm{cm}=3\times10^{-9}\ \mathrm{cm}^{3}$. The heat capacity of Al at 300 K is $C_p=5.82\ \mathrm{cal/K/mole}=24.4\ \mathrm{J/K}/27\ \mathrm{g}=2.44\ \mathrm{J\,K^{-1}\,cm^{-3}}$. The temperature rise neglecting heat conduction is then given by $\Delta T=\mathrm{U/VC_p}=3.6\times10^{-9}\ \mathrm{J}/(2.44\ \mathrm{J\,K^{-1}}\times3\times10^{-9}\ \mathrm{cm^{3}})=0.5$ K. This is the maximum temperature variation. In reality the heat will diffuse during the 1 ns implantation time and the actual surface temperature would be much less than this. The Al heat capacity was taken from the *Handbook of Chemistry and Physics*, 66th ed., edited by R. C. Weast (CSC Press, Boca Raton, 1985).

[35] The maximum slope of a f_{d} vs T curve is $0.03/200\ °\mathrm{C}=1.5\times10^{-4}$ [A. P. Mills, Jr., Phys. Rev. Lett. **41**, 1828 (1978)] which gives a Ps delayed fraction thermally induced by beam impact of $\sim7.5\times10^{-5}$ which is an upper limit and is more than 10 times smaller than the effect we observe.

[36] Large shifts in the work function have been observed on Cu surfaces due to a partial coverage of Cs. [C. A. R. Koymen, K. H. Lee, D. Mehl, A. Weiss, and K. O. Jensen, Phys. Rev. Lett. **68**, 2378 (1992).] The shifts do not simply imply a change in the surface dipole potential, but must involve changes in the width and/or depth of the potential well seen by the surface positrons.

[37] See, for example, P. M. Platzman, in *The Physics of the Two-Dimensional Electron Gas*, edited by J. T. Devreese and F. P. Peters (Plenum, New York, 1986), pp. 97–130.

[38] K. G. Lynn, W. E. Frieze, and Peter J. Schultz, Phys. Rev. Lett. **52**, 1137 (1984).

[39] A. P. Mills, Jr., Appl. Phys. **23**, 189 (1980).

[40] P. J. Schultz, E. M. Gullikson, and A. P. Mills, Jr., Phys. Rev. B **34**, 442 (1986).

[41] Careful measurements via low energy electron diffraction (LEED) might reveal variations in the surface structure, but would not be directly sensitive to hydrogen contamination. On the other hand, positron diffraction might reveal hydrogen on an Al surface: X. M. Chen, K. F. Canter, C. B. Duke, A. Paton, D. L. Lessor, and W. K. Ford, Phys. Rev. B **48**, 2400 (1993).

[42] K. Varga, J. Usukura, and Y. Suzuki, Phys. Rev. Lett. **80**, 1876 (1998).