Desorption of Surface Positrons: A Source of Free Positronium at Thermal Velocities

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A direct measurement is reported of the velocity of positronium (Ps) ejected into a vacuum when 0- to 100-eV positrons (e^+) strike a negatively biased Cu(111) surface. At 30 °C, about half the e^+ form Ps with normal energy component $\overline{E} = 3.4(3)$ eV. At 790 °C, most of the remaining e^+ form Ps but with $\overline{E} = 0.14(1)$ eV, and a non-Maxwellian thermal distribution. We infer that surface-bound e^+ are thermally desorbed to form the extra Ps. These low Ps velocities suggest exciting possibilities for experiments on free Ps.

The discovery[1] that positronium (Ps) is formed efficiently when low-energy positrons impinge on a solid target in a vacuum has made possible a number of measurements[2-4] on Ps free of the effects of the buffer gas[5] which previously was required both to slow the positrons from a radioactive source and to form the Ps. Unfortunately, the free Ps is found to have a ~1-eV energy distribution,[3,6] inconveniently high for many potential applications. Upon heating certain metal surfaces, the efficiency of Ps formation improves[1] with a temperature dependence characteristic of a thermally activated process.[7] This suggests that there may be two mechanisms for Ps formation at a surface; (i) a nonthermal process responsible for the ~1-eV distribution previously measured, and (ii) a thermally activated process which ought[8] to result in a population of Ps with a substantially lower mean energy. In this Letter we report measurements which indeed show the presence of thermal (~0.1 eV) Ps upon heating a Cu(111) surface. Our new measuring technique permits the study of the velocity of Ps formed at any surface including the surfaces of well-characterized samples. The insights thus gained suggest surface conditions which might result in even lower Ps velocities. The achievement of a low-velocity distribution of free Ps has important implications for reducing radiative power density requirements, wall collision effects, and Doppler broadening in precision Ps experiments.

We measure the Ps velocity distribution using a time-of-flight technique adapted from the work of Gidley *et al.*[6] The apparatus (see Fig. 1) consists of a beam of slow positrons in a 3×10^{-10} Torr vacuum, a Cu target on a heater stage, plastic scintillators to detect the Ps annihilation γ rays, and a system of Pb slits to define the annihilation region.

Triplet Ps atoms leaving the target surface travel a certain distance before annihilating via 3γ's with mean lifetime $\tau = 142$ nsec.

By pulsing the positron beam, we establish when the Ps is ejected from the Cu target. We can then use the spatial definition provided by the slits to directly obtain the Ps velocity by its time of flight.

The slow positrons are obtained from a ~50-mCi ^{58}Co source and a Cu(111)+S moderator[9] biased with a time-varying accelerating voltage $V(t)$ to cause -1 μsec portions of the initially 0.25-eV full width at half maximum (FWHM) positrons to arrive at the target all within a few tens of nanoseconds. The ideal voltage pulse is $V(t) = \frac{1}{2} m l^2/t^2$, where l is the distance (2.0-m) between the accelerator electrode and the target, and m is the electron mass. The pulse used in the experiment approximates $V(t)$ for -1.44 μsec $< t < 0.32$ μsec and has a maximum value of +80 V. The time of arrival of the positrons at the target defines $t = 0$. To improve the time profile of the bunch and to eliminate positrons in the 10.23-μsec interval between bursts, the target

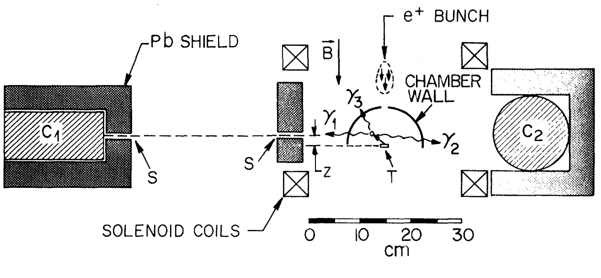

FIG. 1. Positronium time-of-flight apparatus. The target T is a Cu(111) disk (99.999% Cu) 16 mm diam × 1 mm mounted on a Ta heater stage. The solenoidal field B is 150 G along the axis of the positron beam. Counters C_1 and C_2 are 40 and 30 cm high plastic scintillators coupled to EMI 9823 photomultipliers. The 1-cm-wide slits S are centered a distance z in front of the target surface. The Cu crystal is cleaned and coated with $\sim\frac{1}{3}$ monolayer of S by prolonged heating at ~800 °C. (See Refs. 8 and 9.)

was biased at +90 V and gated with < 10-nsec wide − 130-V pulses. A pulse derived from the accelerating voltage starts a time-to-amplitude converter whose output is recorded by a multichannel analyzer. The annihilation of the Ps in the region defined by the slits is signaled by a count in C_1 and distinguished from the singles background by a coincident count in C_2 which generates the required stop pulse.

Lifetime spectra obtained with the slits positioned at $z = 10$ mm and with the Cu target at 30 and 790 °C are shown in Fig. 2(a). The large peaks at $t = 0$ are attributable to the prompt annihilation of $^1S_0$ Ps and also to positrons annihilating in the Cu target. The 5-nsec FWHM of the prompt peak is the net time resolution of the pulsed positron beam and the γ-ray detection system. After the prompt peak there is a distribution of delayed counts from the annihilation of $^3S_1$ Ps in flight. The delayed spectrum obtained with the target at 30 °C shows a more rapid decay than the $^3S_1$ decay rate, because the Ps is moving rapidly through the region seen by the slits. However, with the target at 790 °C we observe (i) a decrease in the prompt annihilation peak, (ii) an increase in the total number of delayed counts, and most significantly, (iii) an increase in the apparent decay time. This is interpreted as evidence that extra Ps is emitted by the heated surface and that the mean energy is lower than that observed for the cold Cu surface. The temperature dependence of the delayed component is shown in the inset of Fig. 2. The data fit an Arrhenius function with an activation energy E = 0.74(15) eV consistent with the value $E_a = 0.76(2)$ eV reported by Mills[8] for Cu(111) with $a \sim \frac{1}{3}$ monolayer of S.

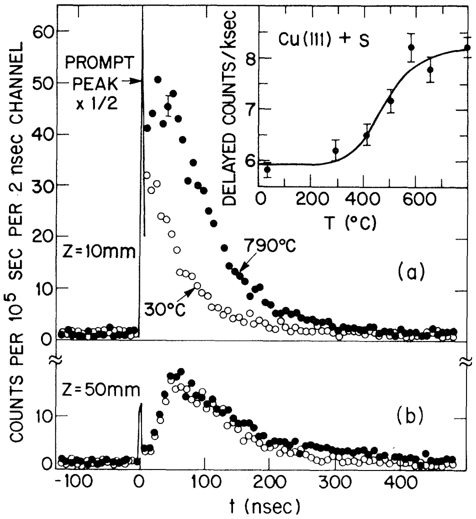

FIG. 2. Time-of-flight spectra of triplet positronium annihilating at z = 10 mm (a) and z = 50 mm (b) in front of the Cu target at 30 °C and 790 °C. Positron bunches arrive at the target at time t = 0 causing the prompt annihilation peaks. The latter have been greatly suppressed by the Pb shielding. The inset shows the total delayed component vs temperature at z = 10 mm obtained with a lower e^+ beam strength. The solid line is the result of a least-squares fit of an Arrhenius function [$f = (f_0 + f_1 z)/(1+z)$, $z = z_0 \exp(-E_z/kT)$] to the data. The χ^2 per degree of freedom for this fitted curve is $\chi^2/\nu = 5.37/3$.

This experiment was repeated by moving the slits forward to $z = 50$ mm [see Fig. 2(b)]. The spectra at 30 °C and 790 °C are now very similar. This is interpreted to mean that few thermally generated Ps atoms are reaching the volume defined by the slits, and that the high-velocity Ps observed in the 30 °C spectra of Fig. 2 is unaffected by the target surface temperature. We can therefore subtract this invariant high-velocity component from our spectra to obtain the spectra attributable to the thermally emitted Ps alone.

It is thus clear that there are two mechanisms for Ps emission. A model[8] which is consistent with this result is that implanted positrons thermalize in the bulk of the Cu crystal and diffuse to the surface. Once at the surface, some of the positrons are emitted as slow positrons, some form Ps with energies up to $\varphi_{\mathrm{Ps}} = \frac{1}{2}$ Ry $- \varphi_- - \varphi_+$, where $\varphi_\pm$ are the electron and positron work functions. Some are trapped in the potential well at the surface with a binding energy $E_b = \frac{1}{2}$ Ry $- \varphi_- + E_a$, where $\frac{1}{2}$ Ry = 6.803 eV is the binding energy of Ps. When the target is heated, some of the surface-bound positrons gain enough energy because of thermal fluctuations to escape from the surface as Ps. This thermally emitted Ps should have a thermal energy distribution as opposed to the few-electron-volt energies expected for the nonthermally emitted Ps. For the surface positrons to escape without an electron is not energetically favorable because[8] $E_b \approx 3$ eV.

To establish accurately the energy distribution of the thermally emitted Ps, we study the 790 °C–30 °C difference spectra shown in Fig. 3. A short time after the positron bunch has struck the target (at $t \approx 1$ nsec) there will be a Ps distribution in phase space $f(z, v_z, 0) = C(v_z)B(z)$, where $C(v_z)$ is the velocity distribution and $B(z)$ is the initial (very narrow) spatial distribution. The Boltzmann equation for f, $df/dt = \partial f/\partial t + (\partial f/\partial z)\dot{z} + (\partial f/\partial v_z)\dot{v}_z = -f/\tau$, has the solution $f = C(v_z)B(z - v_z t)$

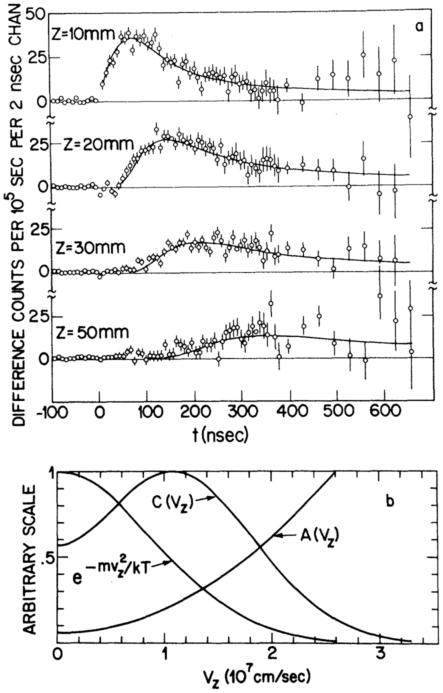

FIG. 3. (a) Difference between the triplet positronium time-of-flight spectra obtained with the Cu target at 790 °C and 30 °C. The data have been multiplied by $e^{t/\tau}$ with $\tau = 142$ nsec to correct for annihilation and the fitted curves have the form of Eqs. (2) and (3). (b) The velocity distribution $C(v_z) = A(v_z)\exp\{-mv_z^2/kT\}$ which fits the data in (a).

$\times \exp(-t/\tau)$, where $1/\tau$ is the annihilation rate and $\dot{v}_z = 0$ because there are no forces. Our experiment measures a count rate

$$S'(z_0,t) = (\epsilon/\tau)\int f(z, v_z, t) R(z - z_0)\,dz\,dv_z, \qquad (1)$$

where ϵ is the detector efficiency and $R(z)$ is the resolution function of the slits, a trapezoidal function experimentally verified to be flat over 1 cm with a 1.5-cm FWHM. The spectra in Fig. 3 have been multiplied by $e^{t/\tau}$ to correct for annihilation. We therefore multiply Eq. (1) by $\exp(t/\tau)$ and, taking the limit $B(z) \to \delta(z)$, we have predicted lifetime curves

$$S(z_0,t) \propto (1/t)\int C(z/t) R(z - z_0)\,dz. \qquad (2)$$

The nth moment of the z component of the velocity, $V_z = z/t$, is given by $\langle v_z^n\rangle = I_{n+1}J_1/I_1J_{n+1}$, where $I_m = \int_0^\infty (z_0/t)^m S(z_0,t)\,dt$ and $J_m = \int_0^\infty (z_0/z)^m R(z - z_0)\,dz$. From the data in Fig. 3 we compute a mean velocity $\langle v_z\rangle = 1.5(1)\times 10^7$ cm sec^{-1} and a mean energy $\bar{E}_z = m\langle v_z^2\rangle = 0.14(1)$ eV for the thermally activated Ps. On the other hand for the nonthermally activated Ps from Cu at 30 °C [Fig. 2(b)] we compute $\langle v_z\rangle = 6.5(3)\times 10^7$ cm sec^{-1} and $\bar{E}_z = 3.4(3)$ eV. The latter value is close to the Ps negative work function $\varphi_{\mathrm{Ps}} = 2.7$ eV for Cu; one does not expect very good agreement because there may be inelastic processes in the Ps formation and because some positrons reach the surface before thermalizing at the low incident energies used here.

To progress further in understanding the velocity distribution of the thermally activated Ps, we assume $C(v_z)$ of the form

$$C(v_z) = A(v_z)\exp\{-mv_z^2/kT\}. \qquad (3)$$

This expression follows from assuming a Boltzmann distribution $\exp\{-E_z/kT\}$ of positronium final states with energy $E_z = mv_z^2$ and density of states proportional to $1/(E_z)^{1/2}$, with $A(v_z)$ accounting for the velocity dependence of the Ps escape probability. By detailed balance, $A(v_z)$ is also the absorption coefficient for Ps incident on the surface with normal component of velocity v_z, since with $\varphi_{\mathrm{Ps}} > 0$ the only inelastic process possible at low v_z is for the positron to become bound at the surface.

The curves in Fig. 3 result from using Eqs. (2) and (3) to fit the difference spectra. The absorption coefficient was taken to be a polynomial in v_z. The best χ square per degree of freedom ($\chi^2/\nu = 217.29/218$) was obtained by fitting[10] with $A(v_z) \propto 1 + (v_z/v_0)^2$, and with free parameters V_0 and T. We find $v_0 = 8.7(1.3)\times 10^6$ cm/sec and $T = 1070(140)$ K in excellent agreement with the measured sample temperature 1063(50) K. On the other hand, a fit using $A(v_z) = \mathrm{const}$ corresponding to a Maxwellian velocity distribution, either results in an unacceptable $\chi^2/\nu = 423.25/219$ if T is constrained to 1063 K, or leads to an unphysical $T = 2660$ K with $\chi^2/\nu = 234.29/218$ if T is unconstrained. We conclude that the Ps velocity distribution is non-Maxwellian and our experiment thus yields the first measurement of the velocity dependence of the Ps absorption coefficient $A(v_z)$ [see Fig. 3(b)]. Since $A(v_z) \neq \mathrm{const}$, the angular distribution of Ps velocities should depart from Knudsen's law,[11] $dN \propto \cos d\Omega$, and experiments to measure the angular distribution directly would be of interest.

In conclusion, our experiment confirms that the thermally activated Ps is formed by thermal desorption of positrons from the surface. Other experiments[8] have shown that the temperature needed to desorb positrons is a strong function of surface material, orientation, and contamination.

Al(100), for example, produces useful amounts of thermally activated Ps at 500 K. Our results imply that the Ps from such a surface should have a velocity spread characteristic of this lower temperature. It is an exciting possibility that suitable surfaces could even be made to yield positronium with energy widths characteristic of cryogenic temperatures.

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Isothermal-Desorption-Rate Measurements in the Vicinity of the Curie Temperature for H_2 Chemisorbed on Nickel Films

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Measurements of the net desorption rate for hydrogen chemisorbed onto nickel films in the vicinity of the Curie temperature are presented. Anomalies are interpreted in terms of anomalous variations in the absolute rate constants for the chemisorption reaction. The results are in qualitative agreement with Suhl's theory for the effect of second-order phase transitions on absolute rate constants.

It is known that the efficiency of reactions heterogeneously catalyzed at surfaces can be modified by bulk phase transitions of the catalyst. Several experimental observations of this phenomenon have been reviewed recently for magnetic catalysts.[1] The theoretical effort to understand this phenomenon had concentrated on the effect of ferromagnetic phase transitions on the rate constants of reaction steps for chemisorbed species.[2] A reaction step of particular interest is desorption from the chemisorbed state to the gas phase, since this can directly affect the overall efficiency of a catalyzed reaction. There has been, however, no detailed measurement of desorption rates in the vicinity of a ferromagnetic transition to compare with theory. An attempt to measure the isothermal desorption rate for H_2 chemisorbed onto Ni in the neighborhood of the Curie temperature was reported in an earlier work.[3] The measurements were, unfortunately, not internally reproducible.

In this note, I present new measurements of the isothermal desorption rate for H_2 chemisorbed onto polycrystalline Ni films. The measurements have been made over a temperature range that spans the Curie temperature of the Ni film, T_C^*. In the vicinity of T_C^* the measured net desorption rate, τ_d^{-1}, undergoes an anomalous decrease and the measured equilibrium constant for the chemisorbed hydrogen, K, displays a large increase. For temperatures above T_C^* the measured activation energy for the net desorption rate, E_d, appears to increase. It is known that the dissociative chemisorption of H_2 on Ni occurs via a mol-