Evidence for Quantum Sticking of Slow Positronium

A. P. Mills, Jr.,(1) E. D. Shaw,(1) M. Leventhal,(1) P. M. Platzman,(1) R. J. Chichester,(1)
D. M. Zuckerman,(1) T. Martin,(2),(a) R. Bruinsma,(2) and R. R. Lee(3)
(1)*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*
(2)*Physics Department, University of California, Los Angeles, California 90024*
(3)*Iguana Systems, 25 Carter Drive, Framingham, Massachusetts 01701*

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We have measured the energy spectrum of positronium (Ps) thermally desorbed from Al(111) surfaces. For sample temperatures as low as 84 K and Ps perpendicular energies between 5 and 50 meV the spectrum is a beam Maxwellian, i.e., a simple exponential. We argue that the surface must be essentially a blackbody for Ps emission, and that we thus have the first example of a system that fails to exhibit the expected perfect reflection of a very slow particle from a cold surface. We suggest that the effect is associated with the breakdown of the perturbation expansion for the Ps reflection probability.

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One quantity characterizing the interaction[1] of a relatively slow neutral particle with a solid surface at a temperature T is the probability $S(\mathbf{k},T)$ that the particle will stick when it impinges upon the surface with momentum $\mathbf{k}$. A question of fundamental importance to quantum many-body theory is: What is the probability $S_0 \equiv S(0,0)$ in the limit of zero velocity and zero T? Given a very weak short-ranged coupling to some type of inelastic channel such as phonon or electron-hole pair emission, it is possible to show that $S_0=0$ due to the vanishing of the scattering particle's wave function at the surface.[2] Higher-order virtual processes, which may be characterized by a dimensionless coupling constant Λ, renormalize the wave function near the surface, increase the effective mass of the particle, and thus enhance the possibilities for sticking. It has been suggested that for Λ of order unity, where the perturbation series breaks down, the inelastic channels will overcome the universal tendency of a particle to quantum reflect from a potential whose characteristic size is much less than a de Broglie wavelength.[3-7]

The basic questions about quantum sticking are as follows: (1) May S_0 ever be greater than 0 for a realizable system? (2) If so, may S_0 have values between 0 and 1 or may it only have the extreme values 0 and 1? (3) In the latter case, might it be possible to vary the conditions of a sample surface so as to exhibit the sudden transition from $S_0=0$ to $S_0=1$ suggested by a recent calculation?[8,9]

Possible systems for experimental study of the quantum-sticking problem would include scattering from solid surfaces using atoms with de Broglie wavelengths $\lambda \approx 100$ Å so that the range of the surface potential and the corrugations of the surface become negligible. The scattering of atomic H and He from He films[10-12] are well-known examples of studies that yield the extrapolated result $S_0=0$ with a nontrivial momentum dependence of $S(\mathbf{k},T)$. In these examples the surface potential is weak, so perhaps the lack of sticking is not surprising. An almost ideal atom in this regard would be positronium (Ps), which is as reactive as H, but has a light mass that allows us to attain $\lambda=100$ Å at a relatively convenient kinetic energy of 7.5 meV. In this paper we present new measurements of the thermal desorption of Ps from which we extract information about S_0 using detailed balance arguments.[2] We argue that $S_0>0$, thus answering question (1) in the affirmative, and explain our result by estimates of the Ps-surface interaction and the breakdown of the perturbation expansion for the reflection probability.

In a typical experiment positrons from a slow e^+ beam[13] are implanted with kinetic energies of several keV into a target. In a good single crystal, thermalized e^+ diffuse about 1000 Å and thus have a high probability of encountering the sample surface. At low temperature the e^+ inside the solid exhibit quantum reflection from the surface potential[14] so that the probability of their escape from the bulk diminishes. However, those that do reach the surface may be captured into a surface state that exists because of the image-correlation potential well seen by a positron just outside the solid. While the surface e^+ state is complex, it is possible to desorb the surface e^+ into the vacuum by heating the solid. The desorbed e^+ form Ps with a thermal energy distribution, and the yield of thermal Ps measured as a function of sample temperature may be used to determine E_B, the Ps surface binding energy.

If Ps on the surface is a free particle in 2D with a single well-defined binding energy E_B, and if all the excited states on the surface can be characterized by the temperature T, and if the density of e^+ in the bulk is low enough, then thermodynamics gives us the total desorption rate,[2]

$$z=(kT/h)\bar{S}(T)\exp\{-E_B/kT\}. \tag{1}$$

Here $\bar{S} \equiv \langle S(\mathbf{k},T)\rangle$ is a suitable average of the sticking coefficient for Ps incident upon the surface from the vacuum. The explicit form of the average will depend on the detailed many-body quantum-mechanical nature of the states of the system. For real, decaying Ps atoms, the desorption rate is in competition with the annihilation rate γ of the surface Ps, leading to a thermal Ps desorption probability[15]

$$f_{\mathrm{Ps}} = z/(z+\gamma) . \tag{2}$$

The predicted energy spectrum of the perpendicular component of the emitted Ps kinetic energy, $E_\perp$, should be a beam Maxwell-Boltzmann distribution times the sticking coefficient $\mathcal{S}(E_\perp,T)$ which is the average of $S(\mathbf{k},T)$ over the transverse components of the Ps velocity, i.e.,

$$dN/dE_\perp = \exp\{-E_\perp/kT\} \times \mathcal{S}(E_\perp,T)/kT . \tag{3}$$

Experiments using a clean Al(111) sample have shown that the temperature dependence of f_{Ps} over the range $300\ \mathrm{K} < T < 740\ \mathrm{K}$ can be explained by Eqs. (1) and (2) if the value $\bar{S}=1$ is used.[16] Furthermore, a measurement of $dN/dE_\perp$ required $\mathcal{S}(E_\perp,T)$ to be constant to within $\pm 10\%$ over the range $10\ \mathrm{meV} < E_\perp < 200\ \mathrm{meV}$ for $T=692$ K. However, we may not necessarily conclude that $S_0=1$, because of the elevated sample and Ps temperatures where $\lambda \approx 10$ Å. In the present study we go to lower T by making use of a submonolayer coverage of oxygen on Al surfaces to cause a decrease in E_B.[17,18]

Our new measurements were made using e^+ generated by an accelerator[19] in 7-nsec pulses containing 5×10^4 slow e^+. The e^+ are implanted with 1-2-keV kinetic energy into an Al target and the Ps energy distributions $dN/dE_\perp$ are measured by a time-of-flight method as previously described.[20] In making these measurements it is important to maintain the sample $T < 300$ K in order to keep the surface atoms from diffusing into the bulk[21] and to properly subtract the component of the spectrum due to the directly emitted Ps.[22]

Our 99.999%-pure Al(111) sample was prepared by electropolishing in a (1:5) perchloric-acid–ethanol mixture and by repeated cycles of Ar$^+$-ion bombardment and annealing at 820 K. Auger spectroscopy *in situ* showed that the surfaces were initially contaminated by less than 1% of a monolayer of C and O. The sample was cooled to 205 ± 5 K and then exposed to 5×10^{-8} torr of O_2 for 15 min. Correcting for the geometry of the vacuum chamber and the location of the leak valve, sample, and pressure gauge, we estimate that the O_2 exposure was equivalent to 24 L ($1\ \mathrm{L}=10^{-6}$ torr sec) and resulted in roughly a one-third monolayer of O on the Al surface. After the exposure the pressure in the vacuum chamber fell below 10^{-10} torr in a few minutes, and below the limit of the gauge (3×10^{-11} torr) about 30 min after starting to cool a 4-K cold shield surrounding the sample manipulator. Time-of-flight spectra were then recorded every 2 min as the sample was cooled over the course of 1 h to 45 K and then warmed for 30 min at a constant rate up to 284 K.

The time-of-flight data due to the thermal component of the Ps were obtained by subtracting a suitably normalized 45-K spectrum from each of the higher-temperature runs. The effect of Ps decay was removed by multiplying the data by $\exp(+t/\tau)$, where τ is the 142-nsec lifetime of o-Ps in vacuum. After subtracting a constant background due to the detection of scattered photons from thermal-Ps decay in the vicinity of the sample, the time-of-flight spectra were converted to energy spectra by multiplying by t^2 and plotting on an energy scale. Figure 1 displays a representative set of energy spectra and the fitted exponential curves. In addition to statistical uncertainties, the total areas under the curves are affected by the opposing temperature dependences of e^+ reflection and diffusion, the former[14] decreasing and the latter increasing the number of e^+ reaching the surface as the temperature is lowered. Taking into account

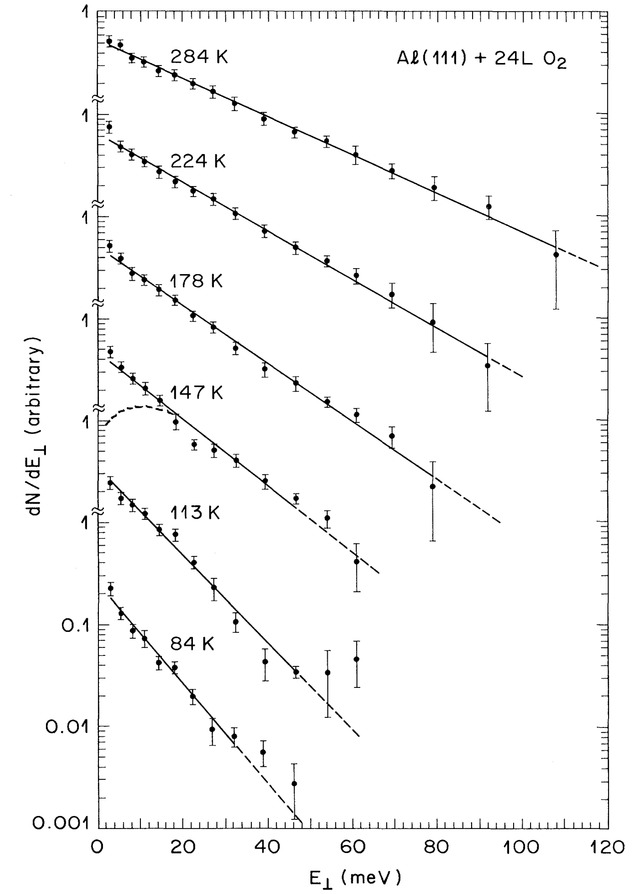

FIG. 1. Spectra of the perpendicular component of the energy of Ps thermally desorbed at various temperatures from an Al(111) surface exposed to 24×10^{-6} torr sec of O_2. The solid lines are fitted exponential functions of $E_\perp$. The dashed line is an example of a spectrum one would have if the sticking coefficient were proportional to $k_\perp$ for $E_\perp < 25$ meV, and constant for greater $E_\perp$.

the lack of thermalization of the implanted e^+, we estimate that such effects produce a systematic shift in the areas roughly the size of the statistical errors. Figure 2 shows the areas of a set of eighteen curves that include the six shown in Fig. 1. The areas of the latter curves are indicated by the solid circles in Fig. 2. An unconstrained fit to the data of Fig. 2 using Eqs. (1) and (2) (dotted curve) yields $E_B = 27 \pm 7$ meV and $\bar{S} = 2^{+2}_{-1} \times 10^{-3}$. If we constrain $\bar{S} \equiv 1$ (solid curve), the optimal binding energy is $E_B = 100$ meV, but the fit is poor. Unlike the previous measurements on a clean Al(111) surface, however, it is possible that the O_2-exposed surface is not uniform, but contains patches of variable E_B. For example, we obtain a good fit to the areas of our time-of-flight curves by using the sum (dashed curve in Fig. 2) of two curves obtained from Eqs. (1) and (2) with $\bar{S} \equiv 1$ and $E_B = 60$ and 120 meV with relative weights in the ratio 1:2. The binding energies of about 100 meV are probably more reasonable than 27 meV, considering the clean-Al value of 300 meV.

Since the energy distributions in Fig. 1 are simple exponential functions of $E_\perp$, we infer that $\mathcal{S}(E_\perp, T)$ is a constant for $E_\perp$ between 5 and 50 meV for $84\ \mathrm{K} < T < 284$ K. If $\mathcal{S}$ were proportional to $k_\perp$ for $E_\perp < 25$ meV and constant for $E_\perp > 25$ meV, by analogy with the internal e^+ reflectivity found in Ref. 14, then $dN/dE_\perp$ would be much smaller than observed at small values of $E_\perp$, as indicated by the dashed curve in Fig. 1. Since the perpendicular projection of the Ps de Broglie wavelength is longer than 100 Å for much of the $(E_\perp, T)$ region explored, it seems safe to conclude that S_0 may be extrapolated from our measurements, and therefore that S_0 is not zero. Our previous result that gave $\bar{S} = 1$ for clean Al, the plausibility of the dashed fit in Fig. 2, and recent theoretical work suggest that $S_0 = 1$ is a definite possibility.

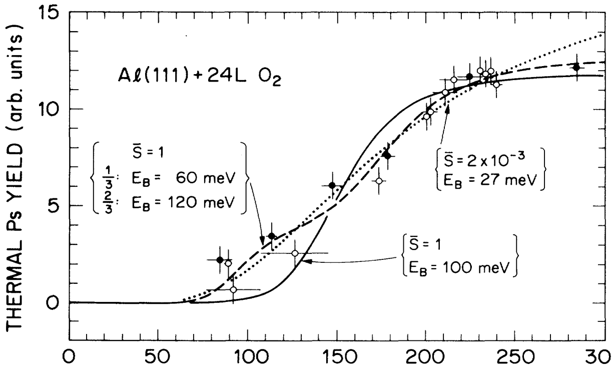

FIG. 2. Total thermal-Ps yield vs sample temperature. The data shown as solid circles correspond to the areas of the curves in Fig. 1. The three fitted curves are discussed in the text.

The coupling of a Ps atom at distances z greater than a few angstroms from a metal surface is due to the fluctuating potential $\phi(\mathbf{r},t)$ generated by the electrons in the solid. The coupling in this case is given by a suitably defined average over the internal coordinates $(\mathbf{x})$ of the Ps atom, i.e.,

$$V = \langle (\mathbf{x} \cdot \nabla\phi)^2 \rangle . \tag{4}$$

The fluctuations of $\phi(\mathbf{r},t)$ associated with the high-frequency surface plasmon degrees of freedom lead naturally to a long-range $1/z^3$ van der Waals potential.[23] At short distances $z < z_c$, the van der Waals potential saturates, and a repulsive potential develops due to overlap of the Ps atom with the surface electrons. Similarly, the important low-frequency fluctuations (particle-hole pairs in the metal) give rise to an interaction potential at large distances given by[24] $V_{\mathrm{int}} = -18(\nabla\phi)^2 a_B^3$, where a_B is the Bohr radius of H. The explicit form of the low-frequency $\phi(\mathbf{r},t)$ is obtained[25] using a simple jellium model of the surface.

A lowest-order distorted-wave Born-approximation calculation of the sticking probability using Eq. (4) [see Fig. 3(a)] shows that quantum reflection reduces the amplitude of the wave function near the surface and *prohibits* sticking, i.e., $\mathcal{S}(k_\perp, 0) \propto k_\perp$. A detailed calculation[25] of the higher-order corrections [see Fig. 3(b)] shows that the dimensionless coupling constant charac-

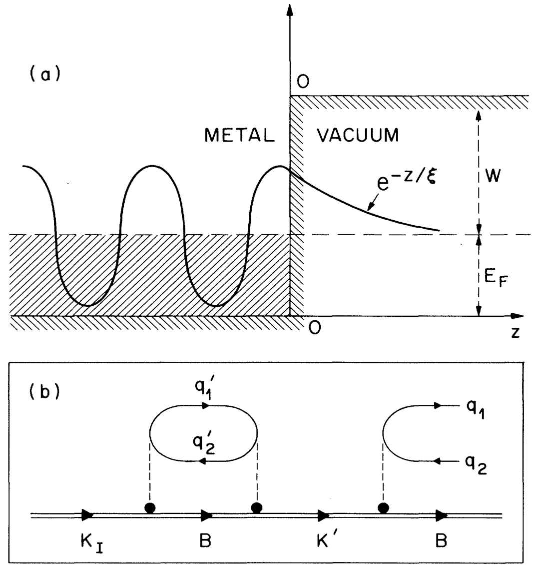

FIG. 3. (a) Schematic of the jellium surface model and (b) the important correction to the leading Born-approximation matrix element for the sticking rate. The double solid line represents Ps labeled by a continuum index K and a bound-state index B. A single line describes electron-hole excitations. A dashed line terminated by a solid dots describes an effective instantaneous momentum-dependent vertex.

terizing the perturbation series for this system is

$$\Lambda \approx 0.28 k_F^3 a_B^3 \left[\frac{z_c}{z_t} \right]^{1/2} \frac{e^2}{r_B} \frac{1}{E_B} , \qquad (5)$$

where z_t is the classical turning point for the bound state, and $r_B \equiv (2mE_B)^{1/2}$. For clean Al, $z_t \approx 2$ Å, $z_c \approx 0.7$ Å, $k_F a_B = 0.92$, $E_B \approx 0.3$ eV, and $\Lambda \approx 1.7$.

Whenever a reactive atom like Ps or H interacts with a metal surface, the coupling constant will be of the form given in Eq. (5). As long as the surface binding energy, the Fermi energy, and the excitation energy of the neutral atom are the same size, Λ will be of order 1 and there is the possibility of quantum sticking. This is *very* different from H on He or He on He where there are no low-lying particle-hole pair excitations and where the bound-state energy and the electronic energies differ by 4 orders of magnitude.

It is interesting to note that Eq. (5) predicts that as the binding energy is lowered, i.e., the wave function moves out from the surface, the coupling constant *increases*. This is related to a much better overlap of the incoming wave function with the bound-state wave function and a not so rapid falloff of the intrinsic coupling to the low-lying excitations. On the other hand, opening a gap in the pair excitation spectrum should prevent sticking. At this point it would be important to verify our conclusions by direct measurements of $\mathcal{S}(E_\perp,T)$ using a beam of slow Ps atoms, and to see if we could decrease the coupling constant continuously in order to observe a possible sudden "transition" to perfect reflection.

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[a] Present address: IBM Watson Research Center, Yorktown Heights, NY 10598.

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