

Positronium formation at physisorbed monolayer surfaces of argon, nitrogen, and oxygen on graphite

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Photon spectra arising from positrons annihilating at surfaces in exfoliated graphite have been measured over a range of temperatures. The role in the annihilation process of physisorbed equilibrium layers of argon, nitrogen, and oxygen has been observed. With argon and nitrogen the formation of orthopositronium is indicated by a three-to-two γ -ray ratio; for nitrogen maximum *o*-Ps was found to occur on completion of one monolayer. In contrast, a Doppler analysis shows that oxygen yields parapositronium. In the case of nitrogen, the results allow the estimation of the coverage, the binding energy of the molecule to the carbon substrate, and the activation energy for the process of Ps emission from the surface traps.

The invention of monochromatic low-energy positron beams¹⁻³ has been important, and early advances are being made in our knowledge of positron interactions at solid surfaces.⁴ For example, the fact that positrons may be trapped in surface states has been confirmed by the observations of enhanced thermally desorbed positronium at increasing temperatures.^{2,3} However, the theory of the positron surface state is still incomplete; indeed, recently reported 2γ angular correlation results⁵ on an aluminium surface indicating an isotropic momentum distribution have not been consistent with either a positron bound by its "image correlation potential"^{6,7} or a positronium atom weakly bound to the surface.⁸ It is clear that more evidence on the behavior of positrons under a variety of surface conditions is needed to resolve the theoretical uncertainties. One such condition is the two-dimensional layer of gas condensed on a known substrate for which positron trapping sites are, in principle, capable of being well characterized. In this paper we show that positrons respond sensitively to monolayer coverages of argon, nitrogen, and oxygen on graphite.

Physisorption is governed by van der Waals forces and information on the growth, phases, and registration of thin films⁹ as a function of temperature has been acquired from isotherm and calorimetry studies^{10,11} neutron diffraction,¹² NMR,¹³ and low-energy electron diffraction¹⁴ methods amongst others. It remains to be seen whether annihilating positrons will provide new insights into the thermodynamics of low-dimensional systems.

Beam studies require UHV to facilitate positron transport and ensure uncontaminated surfaces. Equilibrium monolayer systems are more easily investigated by thermalizing fast positrons within a solid substrate and relying on a large surface-to-volume ratio to ensure that positrons have a high probability of annihilating at the surface. High ratios are possible in powder samples, but they are also obtained in graphite that has been exfoliated—a process that involves the formation of intercalation complexes within layer-structured crystals, and subsequent

heating which explodes the layers apart, to form a uniform substrate of large area. Furthermore, surface oxidation of carbon does not arise.

To study the role of positrons at physisorbed two-dimensional structures on Grafoil,¹⁵ we have measured the annihilation photon spectrum with a germanium detector as a function of sample temperature. A conventional sandwich containing 100 $\mu\text{Ci}^{22}\text{NaCl}$ was prepared. Because of the low density (0.94 g cm^{-3}) of Grafoil, the source was deposited directly at the center of a stack of 12 pieces of Grafoil, each $1 \times 1 \times 0.04\text{ cm}^3$, the number needed to stop all the positrons. After preparation the sample was transferred to a cryostat capable of maintaining controlled temperatures in the range 77–460 K.

The specimen chamber was made of brass which lay in a Dewar of liquid nitrogen. The oxygen and argon gases were introduced in sufficient amounts to ensure they condensed into liquid pools at the bottom of the chamber: hence their equilibrium pressures at 77 K prevailed for all measurements; i.e., 156 and 190 Torr, respectively. The suspended Grafoil sample was maintained at a range of temperatures and the gases were physisorbed on the carbon substrate under equilibrium conditions at the prevailing pressure. In the case of nitrogen four sets of measurements were taken at different pressures.

We have analyzed the spectra in several ways. Specifically, to seek the formation of orthopositronium, which entails 3γ decays, we have recorded the contents of the whole 511-keV photopeak (A) and also of a band of channels (B) in the Compton region corresponding to an energy band at 190–200 keV. Both A and $Y (= A/B)$ will be indicators of the strength of 3γ events, i.e., orthopositronium decay.¹⁶ The Doppler broadening is illustrated with the line-height parameter F , defined as the ratio of the contents of the central 15 channels in the 511-keV photopeak to A ; and in the analysis of the peaks into parabolic and Gaussian components¹⁷ by convoluting the intrinsic resolution (r) of the system determined with the ^{85}Sr line at 514 keV and fitting the expression:

$$f(x) = a \int_{-\infty}^{+\infty} \exp[-(x' - \bar{x})^2 / 2\sigma_G^2] r(x - x') dx' \\ + b \int_{-\sigma_P \sqrt{2}}^{\sigma_P \sqrt{2}} [1 - (x' - \bar{x})^2 / 2\sigma_P^2] r(x - x') dx',$$

from which the widths (σ_G, σ_P) and the relative intensity of the parabolic component (if $> 2-3\%$) can be obtained. It has also been valuable on occasion to analyze instead for two Gaussian components.

Prior to the physisorption measurements we studied the positron-annihilation characteristics of Grafoil in vacuum. Figure 1, which shows the gentle trends of the parameters as a function of temperature, is presented to provide contrast with the physisorption experiments. The only comparable work on such a system has been on positron lifetimes,¹⁸ which found essentially three components, 200, 410, and 1800 ps, interpreted as annihilations in the bulk, in surface-trapped states or quasi-Ps states bound on the surface, and as orthopositronium. We can note that in Fig. 1(b), a declining Y indicates a slow increase in the formation of positronium as the temperature rises above 200 K.

Figure 2(a) shows the results with argon in the chamber; the Y parameter shows a very distinctive minimum at 120 K indicating a maximum of orthopositronium. Figures 2(b), 2(c), 2(d), and 2(e) show the results for nitrogen at equilibrium pressures of 30, 130, 290, 790 Torr, respectively. Sharp minima are again observed, implying maximum *o*-Ps at 105, 119, 127, and 140 K. For both argon and nitrogen only slight variations were observed in the other parameters.

Oxygen is a different case. In Fig. 3(b) the dip in A (Ref. 19) indicates only a modest increase in *o*-Ps at low temperatures. However, the corresponding values of F rise sharply as the temperature declines below 140 K,

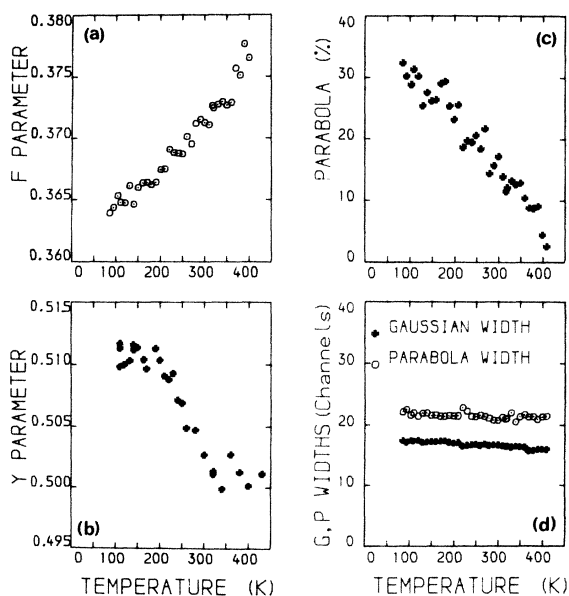


FIG. 1. Grafoil in vacuum: analysis of annihilation photon spectrum as a function of temperature, with parameters described in the text.

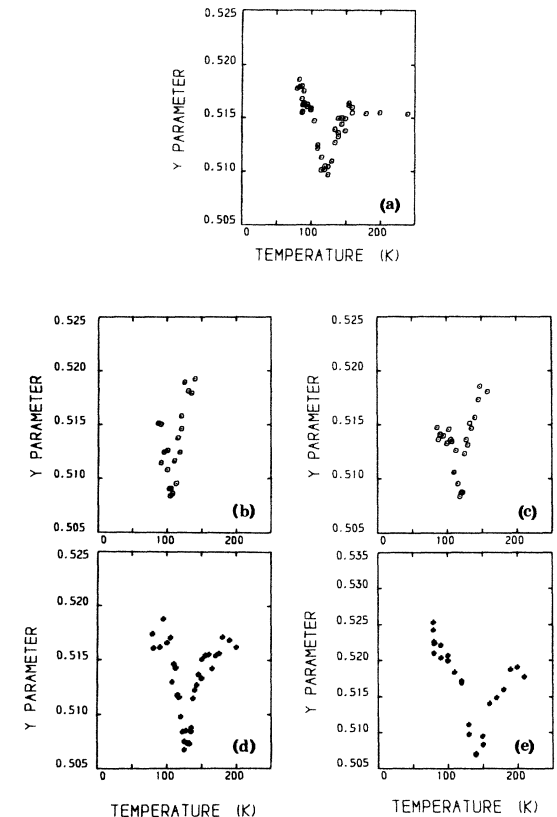


FIG. 2. Formation of orthopositronium: The Y parameter as a function of temperature for (a) Grafoil in argon at 190 Torr; and (b), (c), (d), and (e) Grafoil in nitrogen at 30, 130, 290, and 790 Torr, respectively, showing the displacement of the peak in Ps formation with pressure.

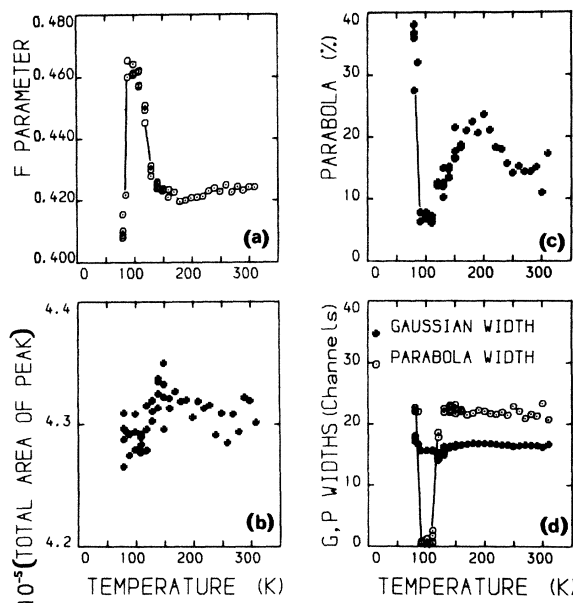


FIG. 3. Results for Grafoil in oxygen at 156 Torr.

reaching a maximum at 100 K, only to drop again at 90 K. The origin of this rise is seen in Fig. 3(d), where a sharp spike of width of only about two channels appears in the Doppler spectrum. This must be parapositronium decaying via 2γ , implying a strong quenching of *o*-Ps by the oxygen, either in a condensed layer or in the gas. We attribute the disappearance of the 2γ spike at 90 K to the suppression of Ps formation by multiple overlayers of oxygen. The 2γ spike is reminiscent of the finding¹⁶ of a reduction in the 3γ fraction for overlayers of chemisorbed oxygen on aluminium and a spin-exchange process leading to *p*-Ps.

The results must be mainly associated with the condensation of gas; it is inconceivable that the temperature alone could affect so discretely the interactions of positrons or the formation of positronium. Although an extensive literature exists on monolayers, the vast majority concerns layers laid down at very low temperatures with low pressures; very little appears comparable with our measurements in a context of high equilibrium pressures.

In the case of graphite in vacuum, the decline in *Y* at high temperatures suggests positrons in relatively deep traps on the carbon surface emerging as Ps. Assuming Ps emission is a thermal process,^{2,3} fitting Fig. 1(b) with $Y = C \exp(-E_a/kT)$ yields a value for the activation energy E_a of 0.07 eV, which is lower than the 0.23 eV proposed in Ref. 18. If $E_a = E_b + \phi_- - 6.8$ eV, where $\phi_- = 5.0$ eV is the electron work function for carbon,²⁰ then the positron binding energy E_b is 1.87 eV which is lower than for most metals.²

For argon the simplest explanation is that the decline in *Y* for temperatures 160→120 K corresponds to enhanced Ps formation as a condensed monolayer develops, and that the rise for 120→80 K coincides with further condensation inhibiting Ps creation. Nitrogen is similar. With oxygen, however, rather than a sharp maximum in Ps production, a plateau appears in the *F*-parameter curve [Fig. 3(a)] which disappears only at 90 K, suggesting that multilayers fill the spaces within the Grafoil and stop all Ps formation at this temperature.

For a fluid monolayer, bound to a substrate and in equilibrium with the adjacent gas, the ideal two-dimensional gas model with the Boltzmann approximation may be applied.⁹ The relation between coverage (*n* molecules m^{-2}) and pressure (*P*) is $P = (nkT/\lambda) \exp(-\epsilon_0/kT)$, if $n\lambda^2 \ll 1$ and where

$\lambda = h/(2\pi mkT)^{1/2}$ and ϵ_0 is the binding energy of the molecule to the substrate. The equation can be applied to nitrogen which is fluid above 85 K for near-monolayer coverages.^{10,12}

Assuming the *Y*-parameter minima for nitrogen in Fig. 2 correspond to the same physical state, i.e., the same value of n_m , in each case, one can fit the four minima to the two-dimensional (2D) gas equation to yield ϵ_0 and n_m . The fitting was most satisfactory: the optimum value of ϵ_0 was 1170 K which agrees reasonably with theory, 1070 K,²¹ 1159 K,²² and for calorimetric measurements, 1177 K.²³

The best $n_m = (7.1 \pm 1.2) \times 10^{18}$ molecules m^{-2} , which can be compared with an estimated density for 100% coverage. Assuming the fluid is "triangularly packed," and taking a value of 4.1 Å for the N_2-N_2 nearest-neighbor distance on a structureless surface,²¹ this n_m corresponds to a coverage of $(103 \pm 17\%)$. We think the alternative view that the positron traps are at a maximum at 50% coverage²⁴ is unlikely in view of the strong mutual repulsion of the N_2 molecules at smaller separations. We therefore conclude that positronium emission increases as the monolayer builds up, but decreases as the bilayer develops.

It is possible to apply the trapping model formula^{2,3} to fit individual peaks on the right-hand slope, i.e.,

$$Y^{-1} = \frac{Y_0^{-1} - Y_\infty^{-1} Z \gamma^{-1} \exp(-E_a/kT)}{1 - Z \gamma^{-1} \exp(-E_a/kT)},$$

in which allowance is made for thermal promotion of Ps emission from traps with an activation energy E_a , and where it is assumed that the rate *Z* is proportional to coverage *n* at temperatures above the minimum in *Y*. Fair fits were achieved; our values averaged at $E_a = 0.035 \pm 0.015$ eV for nitrogen.

We conclude that Ps is emitted from trapped states determined by physisorbed monolayers of atoms or molecules on a regular substrate, and that the finding represents an advance in our prospects of characterizing surface traps for positrons. Furthermore, we show the positron method enables one to explore the creation of fluid monolayers at high temperatures and high pressures.

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