

Positronium production at a carbon-oxygen interface

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Positronium production has been assessed when monolayers of O₂, N₂, and NO have been condensed down to carbon and SiO₂ surfaces. Oxygen on graphite was found to have copious Ps atoms found at complete monolayer coverage. The excitation of the 1-eV electronic O₂ state enables molecules to absorb excess momentum by recoiling into their neighbors in two dimensions.

Positron interactions at surfaces are of immense interest.¹ Perhaps the most fascinating concerns the creation of positronium in which the positron acquires an electron to form a bound system. Detailed attention to particular cases has revealed mechanisms that can be involved. A good example is the study of Sferlazzo *et al.*² of Ps formation at an oriented graphite surface: Their 2- γ angular correlation investigation revealed little Ps at room temperature, but large amounts liberated at elevated temperatures. The lack at low temperatures³ was attributed to the band structure of graphite,⁴ which showed that parallel momentum conservation would forbid electrons at the top of filled bands participating in Ps formation. To explain the high-temperature results, the authors proposed a mechanism in which momentum conservation was satisfied by the emission and absorption of phonons.²

Contemporaneously, positron experiments were being conducted with exfoliated graphite, which acts as an ideal substrate for condensing monolayer surfaces of gases.⁵⁻⁷ It was found that 3 γ /2 γ annihilation measurements,⁷ and from Doppler broadening analysis of 2 γ 511 keV peaks⁸ that ortho Ps and para Ps are produced copiously at graphite surfaces when they are at least partially covered with a condensed monolayer of gas. Subsequently, we have shown⁹ by correlating pressure and annihilation measurements that, in the case of methane, a sharp maximum in Ps production occurs at 50% monolayer coverage, and the evidence suggested that physisorbed molecules, if free to move on the surface, could absorb any surplus electron momentum released in the Ps formation, even at low temperatures. With 100% coverage the molecules would not be free to recoil laterally and hence Ps formation would be inhibited.

In this paper we present evidence indicating a mechanism that invokes spin exchange when positronium is formed at a carbon-oxygen interface. The experimental method was similar to that used in Ref. 7. An exfoliated graphite (grafoil) sample, sandwiching a directly deposited ²²NaCl positron source lay suspended within a chamber whose walls were held at 77 K. Sample temperatures could be controlled in the range 77-450 K. All positrons approached thermal energies in the carbon and, due to the layered structure of grafoil (20 m²/g), a large proportion found themselves arriving at a surface. The photons emerging from the sites of annihilation were ob-

served with a germanium detector with one hour runs; spectral analysis yielded the customary 511 keV Doppler line-height parameter *S*, and the 3 γ /2 γ parameter *R*. Convolution analysis, with allowance for background and intrinsic resolution, into up to five Gaussians revealed the components of the 2 γ 511 keV lines.⁸

The gases O₂, N₂, and NO were employed in turn. In equilibrium, the physisorption of a gas on carbon will be described by the two-dimensional-gas model with the Boltzmann approximation.⁵ The relation between coverage (*n*, mol m⁻²) and pressure (*P*) is

$$P = (n kT/\lambda) \exp(-\epsilon_0/kT),$$

if $n\lambda^2 \ll 1$, where $\lambda = h/(2\pi mkT)^{1/2}$ and ϵ_0 is the binding energy of the molecule to the substrate. Isotherm measurements have yielded 1065 and 1159 K for ϵ_0/k for O₂ and N₂, respectively.^{10,11}

Figure 1(e) shows the dramatic result of cooling graphite in the presence of 760 Torr of nitrogen. As the temperature declines below 200 K, an equilibrium monolayer develops and the sharp rise in *R* indicates the production of Ps,⁷ the major part being ortho Ps emitting 3 photons. By analogy with methane⁹ we think the peak at 140 K corresponding to approximately 50% coverage, and the Ps production ceases at 100% when near 100 K.

With plenty of oxygen present, a puddle will form at the bottom of the chamber at 77 K, and this will maintain a constant vapor pressure of 156 Torr. Figure 1(a) shows the variation in the Doppler parameter *S* as the graphite temperature is lowered indicating the connection between Ps formation and monolayer coverage. para Ps dominates and its existence is demonstrated by the narrowing of the 511 keV spectral line and the consequent rise in *S*. Unlike all other gases studied,^{7,9} condensed oxygen does not manifest a sharp peak in Ps production, but rather still demonstrates a high saturated value at 100% coverage (~105 K). This plateau, clearly seen in the analyzed para Ps component [Fig. 1(c)], also appears with ortho Ps (*R*). As there is no known qualitative difference between the physisorption properties of oxygen and other gases that deny Ps production at 100% coverages, the task is to identify the mechanism that absorbs the surplus momentum with O₂. It may be noted that the variational levels based on the ground state for O₂ and N₂ are virtually the same¹² and are therefore un-

likely to account for the observations here. For O_2 at 90 K, the Ps signal declines so sharply we have to hypothesize it is due to the development of the second layer. It is conceivable that the bilayer induces a phase change in the underlayer and this may play a role, but further work with other methods would be needed to establish the fact.¹³

Early angular correlation measurements by Heinberg and Page¹⁴ showed the distinctive capacity of oxygen strongly to quench positronium from the ortho ($\uparrow\uparrow$) to the para ($\uparrow\downarrow$) state. The ground state of oxygen is $^3\Sigma_g^-$, the triplet state arising from two unpaired electrons with

parallel spins, whereas the first and second excited electronic states are singlet, $^1\Delta_g$ and $^1\Sigma_g^+$ at 0.997 and 1.62 eV above the ground state, respectively.¹² It was recognized that electron-spin exchange might be involved in the quenching, although Ferrell¹⁵ did show that in elastic collisions between Ps and O_2 conversion could take place without it. Deutsch and Berko¹⁶ suggested that the spin conversion occurred via an excited state, which therefore required the Ps to have sufficient kinetic energy. Recently Kakimoto and co-workers^{17,18} have demonstrated for O_2 gas the inelastic process is much faster, with conversion cross sections for the elastic and inelastic cases of

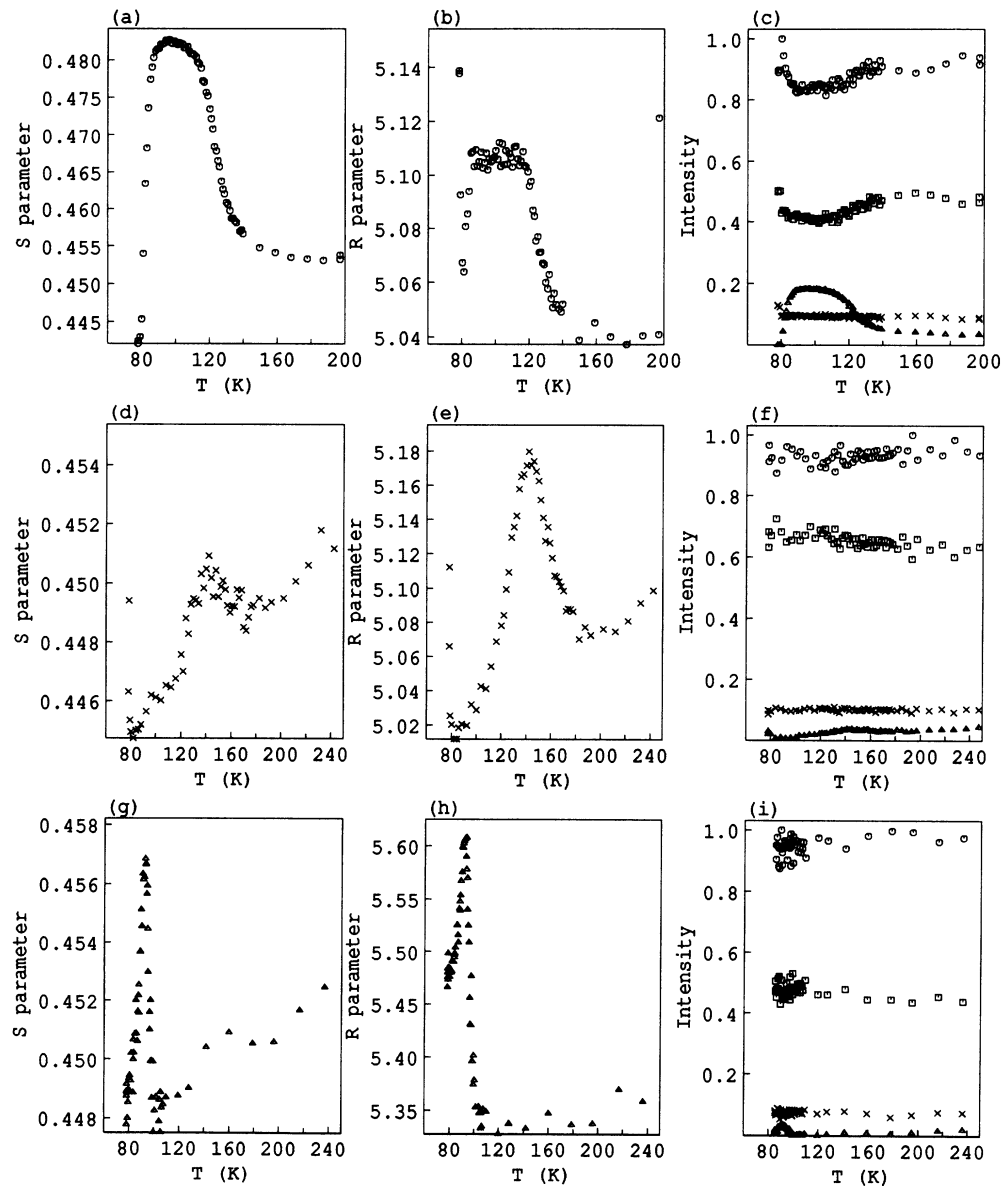


FIG. 1. Results with grafoil; (a,b,c) oxygen at 156 Torr; (d,e,f) nitrogen at 760 Torr; (g,h,i) nitric oxide at ~ 1 Torr. The graphs show that for para Ps (S) and ortho Ps (R) the flat region for O_2 (90–120 K) contrasts with the spikes for N_2 at 145 K and NO at 95 K. Note the percentage changes in R and S . (c,f,i) show the optimum intensities from the convolution analysis with three Gaussians [$\sigma_{G1}=12.2$ ch (grafoil) (○); $\sigma_{G2}=3.5$ ch (slow para Ps) (△); $\sigma_{G3}=21.3$ ch (chamber wall) (×)] and one parabola [$\sigma_p=16.5$ ch (grafoil) (□)]. Intensity is given in arbitrary units.

10^{-19} and 10^{-17} cm^2 , respectively.

To test the role of unpaired electrons we have experimented with nitric oxide, which has a single unpaired electron, a doublet $^2\Pi$ ground state, and is known to engage in spin conversion of ortho Ps even more strongly than oxygen.¹⁹ Figures 1(g) and 1(h) show, however, that a very sharp Ps production peak occurs for NO on grafoil so the O_2 anomaly is not merely a question of the Exclusion Principle.

We are thus led to suggest that the grafoil results concern the unique feature of oxygen—the low-energy first excited state at 1 eV (cf. ~ 5 eV) for NO (Ref. 12), and this state must be involved in the Ps production. Although Sferlazzo *et al.*² observed an average free Ps kinetic energy of only 0.6 eV it may be that the presence of the monolayer alters the work function and allows a release of the necessary energy. It is paradoxical that the excitation of the 1 eV O_2 state exacerbates the problem; additional momentum must be absorbed.

To aid our interpretation we have taken similar measurements with O_2 and N_2 , at various pressures, on silica powder (70 Å diameter). It is known that Ps forms in silica and fast Ps emerges from the SiO_2 surface with 3.26

eV.²⁰ Figure 2(a) shows the gentle linear decline in S for oxygen as temperature diminishes, and the curves for different pressures confirm the reduction in both para Ps and ortho Ps with the onset of the monolayer. This gentle decline is quite different from the sharp drop for O_2 on carbon at 90 K and must therefore be of different origin.

In Fig. 2(c) we note how the fast para Ps (7.4 channels width) diminishes as O_2 is laid down on the surface. The narrower 2.5 channel component corresponds to ortho Ps cooled in the O_2 gas prior to conversion to para Ps, and this also diminishes. These results can be contrasted with N_2 for which Fig. 2(f) shows that the fast para Ps component (7.4 ch) remains virtually constant as N_2 layers are laid down; ultimately it disappears at 80 K when the grafoil interleaf spaces are filled with N_2 and we observe the rise of the sharp peak (3.1 ch) characteristic of annihilation in liquid N_2 .²¹ Thus Ps may emerge from a nitrogen surface but is inhibited at an oxygen surface. This is in agreement with the suggestion originally advanced by Paul,²² that in liquid oxygen, where no sharp para Ps spike is seen, a bound PsO_2 state may be quickly formed in which case the positron will annihilate by pickoff at a

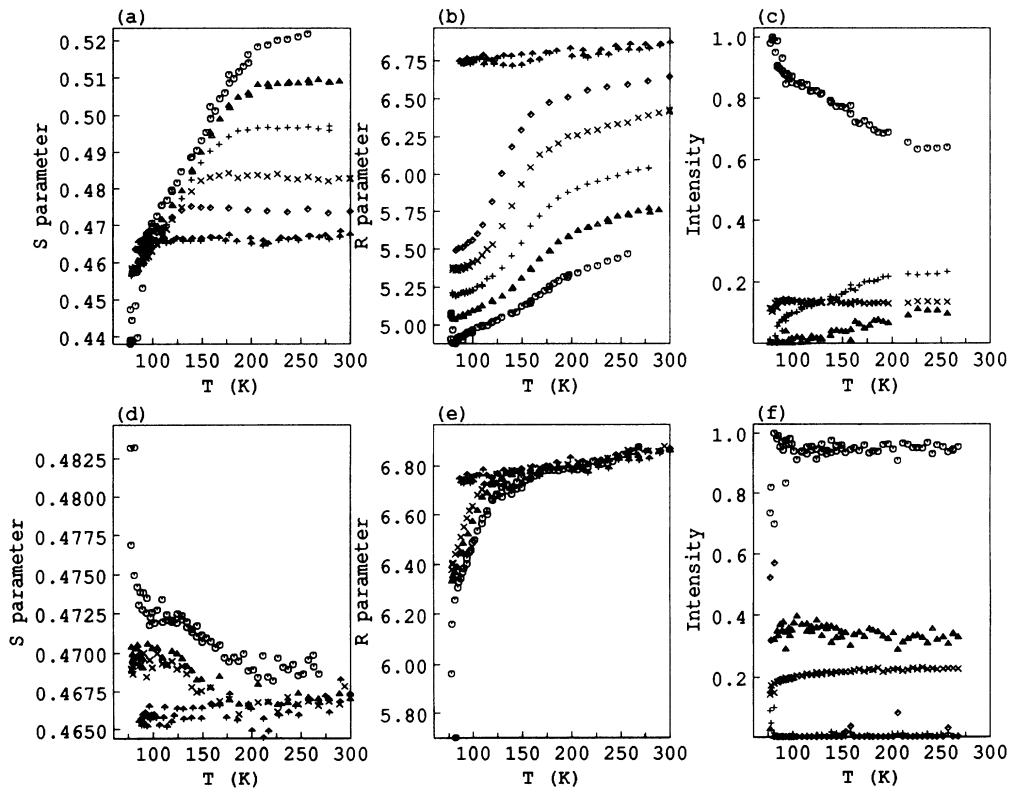


FIG. 2. Results with SiO_2 powder; (a,b) oxygen at 156 Torr (\odot), 90 Torr (\triangle), 41 Torr ($+$), 12 Torr (\times), 4 Torr (\diamond) 0 Torr (vacuum) (\clubsuit); (d,e) nitrogen at 760 Torr (\odot), 300 Torr (\triangle), 100 Torr (\times), and 0 Torr (\spadesuit). In the convolution analysis (c,f) four Gaussians were used for O_2 [$\sigma_{G1}=21$ ch (chamber wall) (\times); $\sigma_{G2}=11.6$ ch (SiO_2 and liq. O_2) (\odot); $\sigma_{G3}=7.4$ ch (fast para Ps) (\triangle); $\sigma_{G4}=2.5$ ch. (slow para Ps) ($+$); and five Gaussians for N_2 [$\sigma_{G1}=21$ ch (chamber wall) (\times); $\sigma_{G2}=11.6$ ch (SiO_2) (\odot); $\sigma_{G3}=7.4$ ch (fast para Ps) (\triangle); $\sigma_{G4}=3.1$ ch (slow para Ps) ($+$); and $\sigma_{G5}=9.5$ ch (liq. N_2) (\diamond)]. The fast para Ps declines for O_2 but remains almost constant for N_2 except at the lowest temperature when it is thermalized in the liquid N_2 and the narrow component ($+$) rises steeply. Intensity is given in arbitrary units.

rate much faster than the para Ps annihilation rate. This is confirmed in Fig. 2(a) for SiO₂ grains where the curve for *s* with maximum O₂ at the lowest temperatures descends below the vacuum value due to annihilation via pickoff with a much Doppler-broadened peak, as in liquid O₂.²¹ In contrast, in the grafoil case, because para Ps remains high, the Ps must be ejected from the O₂ monolayer surface.

To summarize, we find that for oxygen on the basal plane of carbon, positronium is produced and liberated at

100% monolayer coverage but is not when a bilayer is condensed down. The production involves spin exchange via the excitation of the 1 eV first excited state, and the conclusion must be that excited molecules of O₂ recoil into their neighbors in two dimensions.

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