

Evidence for Positronium Formation Assisted by Molecular Recoil at a Graphite Surface Covered with a Semilayer of Methane

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Positrons annihilating at a physisorbed monolayer of methane on graphite have been studied. Photon spectra reveal that positronium is formed and pressure measurements indicate that it rises to a sharp maximum at 50% coverage. The data are in accord with the hypothesis that the Ps formation at the graphite surface is assisted by molecular recoil.

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Positronium—the bound electron-positron pair—is a fascinating system, and its creation and interactions with matter demand investigation.¹ Currently, positronium (Ps) formation at metallic and insulating surfaces is under intense scrutiny. Initially, Ps was observed to be emitted from metallic samples bombarded with low-energy positrons.² Lately, time-of-flight spectroscopy has revealed that the Ps energy distribution from a number of metals is consistent with the hypothesis that Ps formation leaves behind a single electron hole in the conduction band of the metal.^{3,4} For insulators, Ps emission was first observed from powders by lifetime experiments,^{5,6} and recently measurements have been made on ice.⁷ Time-of-flight spectroscopy on quartz and magnesium oxide, subjected to positron bombardment, suggested Ps formation mechanisms involving delocalized Bloch-wave Ps, weakly bound Wannier-type Ps states, and escaping epithermal positrons.⁸

Associated with the formation of Ps is the question of whether Ps can be trapped at surfaces. Most of the work so far has concerned Ps emitted from surfaces, but evidence for physisorbed Ps at the surface of quartz has been found.⁹ Platzman and Tzoar¹⁰ have considered the possibility that Ps may be physisorbed at a jellium surface and we can expect more theoretical work. Apart from large surfaces, there is also the important question of Ps confined in voids.¹¹

Of special interest has been the carbon surface, with several groups¹²⁻¹⁴ finding a curiously low level of Ps formation. However, new angular-correlation measurements¹⁵ have provided convincing evidence that Ps appears abundantly at higher temperatures, supporting the hypothesis that the production is aided by phonon processes.

In 1986 we showed¹³ that positronium may be formed when monolayers of the gases Ar, N₂, and O₂ are condensed on graphite. With improved experimentation, including definitive pressure measurements, we now report that Ps production occurring at low temperatures in the presence of physisorbed methane molecules rises to a sharp maximum at half coverage.

When a solid surface is cooled in the presence of a gas, condensation may lead to the development of a physisorbed monolayer, determined by van der Waals forces. Exfoliated graphite, commercially known as Grafoil, is an ideal substrate in that, being comprised of compressed leaves of carbon oriented in the basal plane, it presents a huge surface area ($\sim 20 \text{ m}^2 \text{ g}^{-1}$). Such a system is favorable for positron measurements, and the fact that any physisorbed equilibrium monolayer is clean is an advantage. The density of Grafoil is about 1 g cm^{-3} and about half that of graphite, 2.3 g cm^{-3} . The surface area therefore implies leaves of carbon, on an average 450 \AA thick, with $550\text{-}\text{\AA}$ spaces between leaves.

The specimen chamber was made of brass which lay in a Dewar of liquid nitrogen.¹³ The suspended Grafoil sample was maintained at a range of temperatures above 77 K . Prior to the introduction of fixed quantities of 99.995% pure methane, the sample was held at 470 K in vacuum for 24 h. The methane was physisorbed on the carbon substrate under equilibrium conditions at the prevailing pressure which was recorded with a sensitive transducer gauge.

In the temperature and pressure regime of main concern here, methane physisorbed onto carbon will be a two-dimensional gas.¹⁶ For such a system, in equilibrium, the ideal two-dimensional-gas model with the Boltzmann approximation holds.¹⁷ The relation between the coverage (n , mol m^{-2}) and pressure (P) is $P = (nkT/\lambda) \exp(-\epsilon_0/kT)$, 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.

The principle of the experiment is that positrons from $100 \mu\text{C}$ of $^{22}\text{NaCl}$ immersed in a Grafoil sandwich¹³ approach thermal energies within the carbon leaves to find themselves at a surface. To investigate their subsequent behavior, the Doppler-broadened 511-keV annihilation peak and the $2\gamma/3\gamma$ ratio have been measured with a germanium detector as a function of temperature. The results yield information on the intensities of annihilations from *p*- and *o*-Ps.

Figure 1 shows the change in $2\gamma/3\gamma$ ratio as the tem-

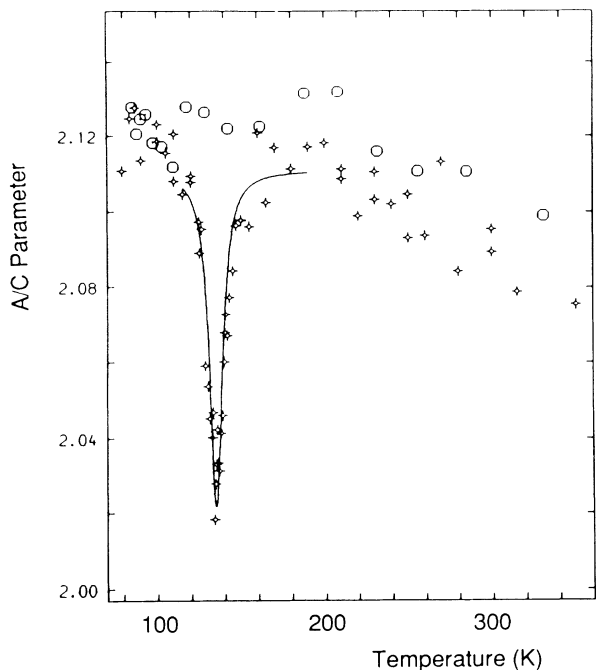


FIG. 1. The production of orthopositronium as a function of temperature in the presence of methane. For comparison the circles show values obtained with the chamber evacuated.

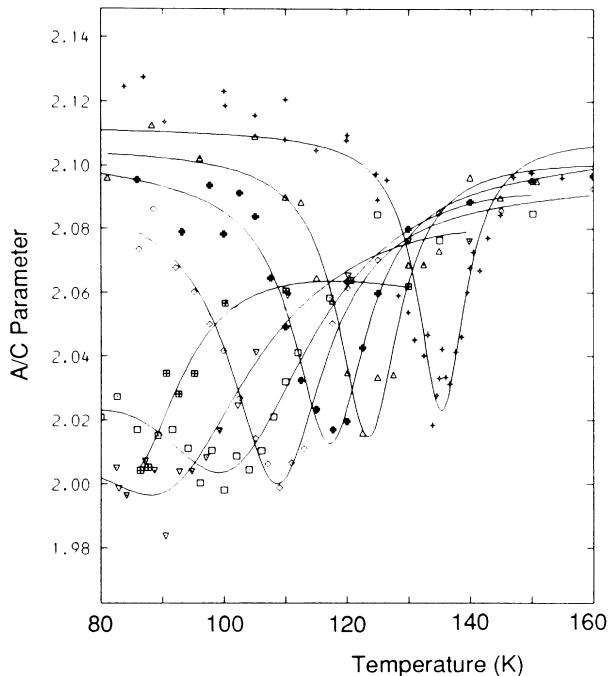


FIG. 2. With different prevailing pressures (see Fig. 3) the temperatures of monolayer development vary and consequently alter the point of maximum *o*-Ps formation.

perature is reduced and condensation increased. The ratio is given by the counts in the 511-keV peak (*A*) divided by the counts in a band of 100 channels (*C*) in the spectral region at about 300 keV. With merely vacuum present in the chamber no change is seen in *A/C* between 80 and 200 K implying negligible variation in Ps formation at the bare carbon surface. The introduction of methane causes a steep dip in *A/C* as condensation begins to develop the physisorbed monolayer. The production of *o*-Ps reaches a maximum and sharply returns to its original value.

Altering the amount of gas in the chamber in effect alters the resultant pressure at any sample temperature. From the equation above one expects a monolayer to build up at a lower temperature at a reduced pressure. Figure 2 shows how the $2\gamma/3\gamma$ peak responds, moving to lower temperatures as expected. If one assumes that the minimum of the peak occurs at the same monolayer coverage in each case, a plot of the chamber pressure at the minimum against temperature takes the form shown in Fig. 3. The 2D-gas equation fitted to the points yields a value for the absorption energy ϵ_0 of 1599 K, which compares reasonably with the values of 1660,¹⁸ 1460,¹⁹ and 1610 K²⁰ obtained by isotherm measurements. The peak heights in Fig. 2 show that there is no significant temperature dependence.

In addition to the $2\gamma/3\gamma$ ratio, the Doppler broadening of the 511-keV peak was recorded. To estimate the amount of *p*-Ps produced, we analyzed the peak for three

components.²¹ Figure 4 shows how a third narrow component appears at 135 K; 3% of the 2γ annihilations are from *p*-Ps. This suggests a maximum of up to 12% of

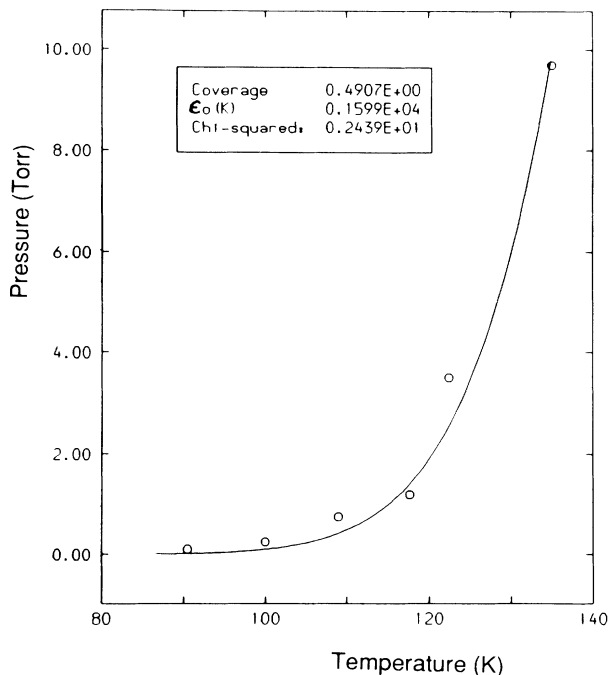


FIG. 3. Plot of the methane pressure at each minimum shown in Fig. 2.

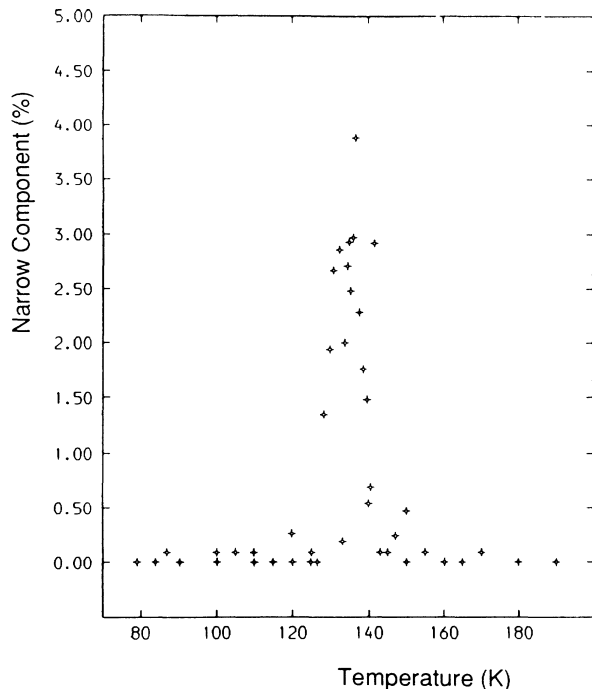


FIG. 4. Results of a three-component analysis of the 511-keV peaks associated with the methane monolayer development at 10 Torr. The appearance of a third narrow component (four channels wide) reveals the creation of parapositronium.

the positrons forming positronium.

The pressure of methane in the chamber was recorded for each measurement. Figure 5 shows how it varies with the production of orthopositronium. The shape of the curve is reminiscent of isotherm studies of condensation: A step appears as a consequence of the pressure dropping during the buildup of a monolayer, only to flatten again at the lower temperatures when the layer is complete. The variation in Ps formation appears to be directly related to coverage, maximizing at the point of inflection indicating 50% coverage.

In 1986, with nitrogen,¹³ we suggested that maximum *o*-Ps occurred on completion of a monolayer. With a similar system, Jean, Yu, and Zhou²² concluded from lifetime measurements that the Ps intensity remained fixed but that a second lifetime component due to surface positron annihilations reached a maximum at 50% coverage. On the basis of our new results, and accepting that complete wetting occurs,¹⁶ we now agree that the peaks correspond to maximum surface unevenness (50%) but, of course, we hold that the effect is due to Ps formation. To verify this conclusion we conducted a separate isotherm measurement at 110 K on the Grafoil specimen.

With 100% coverage, the fluid film is essentially free molecular methane. Photoelectron spectroscopy shows that it requires at least 12.7 eV to remove an electron from CH₄,²³ and it is clear the 6.8-eV Ps binding energy available is insufficient to overcome this barrier. Thus no

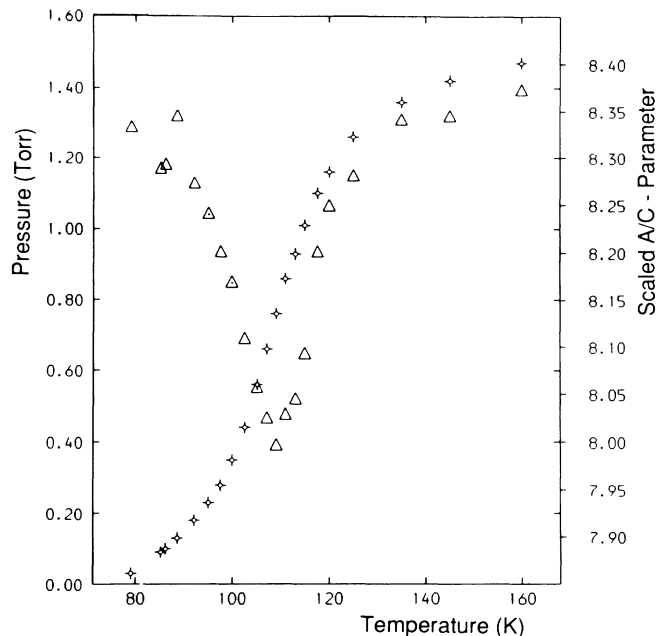


FIG. 5. Simultaneous pressure and A/C values as a function of temperature and, hence, monolayer development.

positronium formation is to be expected from thermal positrons.

The amount, or lack, of Ps formation is identical for zero and 100% coverage as indicated in Fig. 1. For zero coverage the surface is graphite, and for Ps emission it is necessary that $6.8 \text{ eV} > \phi_{e+} + \phi_{e-}$. Hence with $\phi_{e-} = 4.7 \text{ eV}$,^{24,25} and $\phi_{e+} = 1.4 \text{ eV}$,^{15,26} positronium is expected. However, it has been pointed out¹⁵ that the electronic structure of graphite²⁷ shows that electrons within 0.6 eV of the Fermi energy are at the top of filled bands around the zone edges. Parallel-momentum conservation prevents these electrons from participating in a simple one-electron-hole Ps production process, but at higher temperatures this may be overcome by the emission and absorption of phonons.¹⁵

The present results with physisorbed methane at low temperatures therefore indicate that it is the molecular recoil that conserves momentum and hence promotes the formation of Ps. That is, Ps is formed when a thermalized positron arrives at the carbon surface to combine with an electron near the zone edge, the electron momentum being taken up in the recoil of an adjacent molecule. The probability of absorption of the excess electron momentum is greatest when the fluid monolayer is at half coverage, maximizing the possibility of a free recoil interaction as complete wetting occurs.¹⁶

In conclusion, we provide evidence for a new mechanism for positronium emission. Further work is likely to lead to advances in our understanding of physisorption characteristics including the nature of film fluidity, and also possibly of surface electron momentum states.

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