

Positron Annihilation Study of Capillary Condensation of Nitrogen Gas in a Mesoporous Solid

N. J. Wilkinson, M. A. Alam, J. M. Clayton, R. Evans, H. M. Fretwell, and S. G. Usmar
H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom
 (Received 20 July 1992)

Positronium annihilation spectroscopy has been used to study capillary condensation of nitrogen adsorbed in mesoporous VYCOR glass. The temperature and pressure dependences of the relative change in the $3\gamma:2\gamma$ annihilation ratio are reported. Both isobars and isotherms exhibit features which are associated with a shifted gas-liquid transition. The isotherm data suggest that pore filling occurs via progressive layer formation at the pore surface followed by an abrupt gas-liquid phase transition at some pressure below the bulk saturated vapor pressure. Such a picture is consistent with the theoretical treatment of adsorption in individual pores.

PACS numbers: 64.70.Fx, 36.10.Dr, 78.70.Bj

Although the adsorption of gases on porous substrates has been the subject of investigation [1] since the beginning of this century, it is only in recent years that any fundamental understanding of the underlying physical processes has emerged. One striking phenomenon that is observed for a wide variety of substrates is the capillary condensation of the adsorbed gas to a dense liquidlike state filling the pores at a pressure which is less than the bulk saturated vapor pressure (P_{sat}). Theory suggests that this phenomenon corresponds to a shift of the bulk condensation transition arising from finite-size effects. Adsorption isotherm measurements [1,2] (adsorbed mass versus pressure) register the transition as a rapid increase in the mass adsorbed, with accompanying pronounced hysteresis. Neutron scattering studies of water vapor in porous VYCOR glass [3] exhibit hysteresis which has also been associated with a shifted gas-liquid phase transition. However, the precise nature of capillary condensation and the interpretation of the associated hysteresis in real porous materials remain rather controversial issues [2]. Here we present the first data which demonstrate definitively that positron and/or positronium annihilation spectroscopy [4] can be used to study capillary condensation in mesoporous materials and provide direct information about the pore environment.

Under favorable circumstances [4(a)], i.e., in nonmetallic materials such as glasses and polymers and many liquids and gases, a positron will form positronium (Ps). Statistically, three-quarters of the Ps will be ortho-Ps (o -Ps) and one-quarter para-Ps (p -Ps). In a vacuum, the o -Ps decays via the emission of 3γ photons and has a lifetime of ≈ 140 ns. p -Ps has a lifetime of 125 ps and annihilates into 2γ photons. In anything other than vacuum ($\leq 1 \times 10^{-3}$ Pa) o -Ps has, because of its relatively long lifetime, a finite probability of interacting [4(b),4(c)] with the surrounding medium. The consequence of such an interaction is to facilitate 2γ -photon decay, a process called quenching [4(b),4(c)], and to shorten the o -Ps lifetime. The extent to which a surrounding medium facilitates o -Ps quenching will obviously depend on the density of the medium. The probability of such quenching can be

monitored by measuring the relative changes in the $3\gamma:2\gamma$ annihilation ratio.

A fraction of positrons entering a solid which contains interconnecting pores would be expected to reach the pores, form Ps within them, and subsequently annihilate. In small (radius $R < o$ -Ps mean free path) pores some fraction of the o -Ps will undergo 2γ annihilation via quenching with the pore walls. The introduction of high-density gas into the pores would, via o -Ps quenching in the gas, increase the 2γ component of the annihilation spectrum. A further and substantial increase of the 2γ contribution would result if a gas-liquid transition occurred within the pores since the average density of the confined fluid is then much larger. Thus, measurement of the $3\gamma:2\gamma$ ratio of the positron annihilation spectrum for such a system provides a novel probe for phase behavior of fluids in confined geometries and should make a significant contribution in the further understanding of the underlying physics and chemistry of "capillary condensation" and related adsorption phenomena.

For the purpose of the experiments a small pressure cell of volume ≈ 110 mm³ was designed together with associated specimen cooling, heating, and evacuation facilities. The samples were commercially available VYCOR glass containing cylindrical interconnecting pores of average radius $R \approx 20$ Å occupying $\approx 30\%$ of the total volume [5]. The experiments were performed using 99.999% pure nitrogen. Once in the pressure chamber, the specimens were subjected to evacuation (at a chamber pressure of 10^{-7} torr) for ≈ 24 h before nitrogen gas was introduced. Both isobars and isotherms were measured. Most of the experiments performed were measurements of the energy distribution of the annihilation photons. The data were analyzed using a number of parameters derived from these distributions. Here, we present results for a parameter $N(3\gamma/2\gamma)$ representing the total counts in the region 340–490 keV divided by the total counts in the region 491–541 keV. This parameter provides a measure of the relative changes in the $3\gamma:2\gamma$ annihilation ratio. The annihilation energy measurements were supplemented by positron lifetime experi-

ments.

In Fig. 1(a) we present the temperature dependence of $N(3\gamma/2\gamma)$ along an isobar (10 bars) for bulk nitrogen and nitrogen gas confined in the pores of VYCOR glass (henceforth referred to as capillary confined nitrogen). Here a sharp step in $N(3\gamma/2\gamma)$ is apparent at ≈ 107 and ≈ 112 K for bulk and capillary confined nitrogen, respectively. For the bulk data this temperature corresponds, within experimental error, to the gas-liquid phase transition at this pressure (104 K [6]). Thus, the step observed for the capillary confined fluid is interpreted to be the result of a shifted gas-liquid phase transition. The smaller step observed in $N(3\gamma/2\gamma)$ for bulk condensation results from the fact that without the VYCOR present in the pressure cell a large fraction of the positrons reach and subsequently annihilate from the cell walls. Thus the fraction of positrons forming Ps (in the gas) is significantly reduced, leading to a lower initial value of $N(3\gamma/2\gamma)$ for this source cell configuration.

A similar Ps annihilation parameter was used by Rice-Evans *et al.* [7] in studies of adsorption of nitrogen on Grafoil. They observed a peak in the 3γ annihilation at half-monolayer coverage during monolayer formation. In VYCOR specimens, we also observe a peak in $N(3\gamma/2\gamma)$. At ≈ 1 bar the peak occurs at ≈ 150 K, the same as reported by Rice-Evans *et al.* [7] for nitrogen at 1 bar in Grafoil. It is clear that the sharp steps in $N(3\gamma/2\gamma)$ reported in this Letter are not due to monolayer formation but must be due to another mechanism which we identify as capillary condensation. It is also important to note that in experiments with the VYCOR in vacuum no significant changes in $N(3\gamma/2\gamma)$ were observed over the same temperature range, discounting the possibility that the observed changes are due to changes in the VYCOR itself.

Complementary lifetime studies of capillary confined

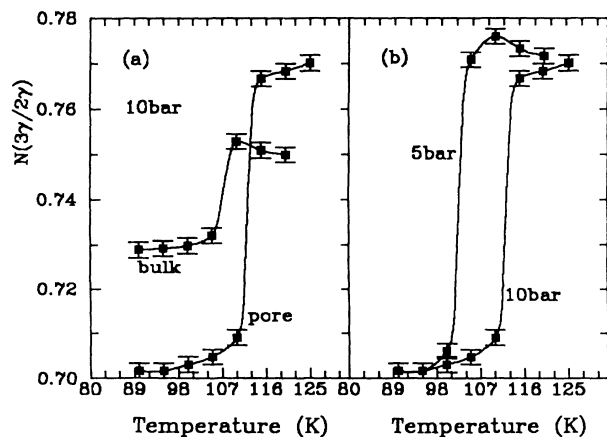


FIG. 1. Temperature dependence of the Ps annihilation parameter $N(3\gamma/2\gamma)$ (a) for capillary confined and bulk nitrogen at 10 bars and (b) for capillary confined nitrogen at 5 and 10 bars.

N_2 , at $P=10$ bars and $T \approx 105$ K, give further support to the contention that the step in $N(3\gamma/2\gamma)$ observed for capillary confined fluid results from a (shifted) gas-liquid transition. Here a long lifetime component of ≈ 12 ns, which is similar to that reported [8] for *o*-Ps in bulk liquid N_2 at ≤ 77 K, was observed. At room temperature and 1 bar, capillary confined nitrogen gas was found to have an *o*-Ps lifetime of $\approx 75 \pm 5$ ns. The observed *o*-Ps lifetime for bulk nitrogen gas [9] is ≈ 70 ns.

Figure 1(a) suggests that at 10 bars pressure, the gas-liquid transition temperature in the pores is about 4–5 K higher than the corresponding bulk transition temperature. This shift in temperature can be estimated from the Kelvin equation [10] $\Delta T/T_{co} \approx 2\sigma_l/RL\rho_l$, where ΔT is the shift from the bulk gas-liquid coexistence temperature T_{co} , σ_l is the liquid-gas surface tension, R the average pore radius, L the latent heat of evaporation, and ρ_l the liquid density at bulk coexistence. The Kelvin equation is derived by balancing the surface and bulk contributions to the total free energy of the confined fluid and is strictly valid in the limit of large radius R . Using this relation one obtains a value of $\Delta T \approx 3.5$ K at 10 bars which is not too different from our observed value.

Figure 1(b) shows $N(3\gamma/2\gamma)$ as a function of temperature for capillary confined nitrogen in VYCOR for two different pressures. We observe the expected decrease in the transition temperature as a function of decreasing pressure. The shift in temperature is compatible with the expected phase diagram for the capillary confined gas. In Fig. 2 we present a few experimental points derived from measured isobars to illustrate the shift of the condensation line (vapor pressure curve) when nitrogen is capillary confined.

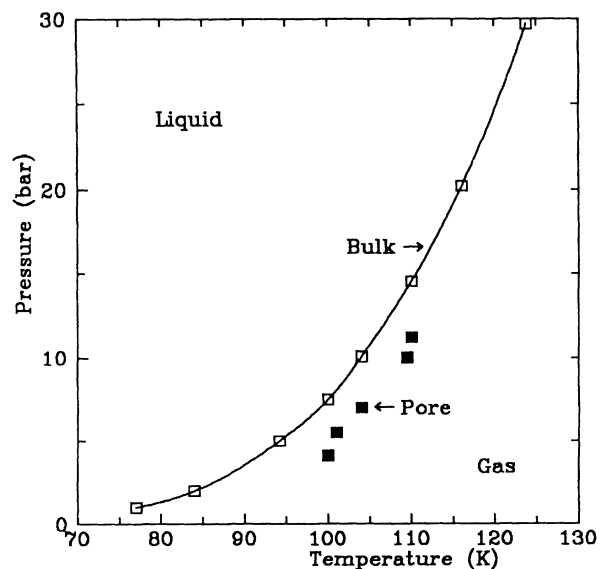


FIG. 2. Partial phase diagram for bulk (vapor pressure data taken from Ref. [6]) and capillary confined nitrogen [deduced from the step in $N(3\gamma/2\gamma)$].

The measured isotherms for capillary confined nitrogen exhibit striking behavior. In Fig. 3 we present a set of isotherms measured at 100, 103, and 110 K. In each case the measurements were carried out in the pressure range between $0.1P_{\text{sat}}$ and $1.2P_{\text{sat}}$. Experiments were repeated through several cycles of increasing and decreasing pressures. Here, again, we observe the sharp drop in $N(3\gamma/2\gamma)$ which is interpreted as the "gas-liquid" transition for capillary confined nitrogen. On the gas side of the transition, $N(3\gamma/2\gamma)$ exhibits a linear decrease as a function of increasing pressure. In addition, we observe the following features: (i) At each temperature, the transition occurs at pressures significantly less than P_{sat} . (ii) The value of P/P_{sat} at which the transition is observed decreases with decreasing temperature. (iii) A significant hysteresis is observed in the isotherms during increasing and decreasing pressure cycles. During the decreasing pressure cycle the liquid-gas transition occurs at a considerably lower pressure and the step in $N(3\gamma/2\gamma)$ is somewhat steeper. (iv) Although not shown in the figure, a gradual decrease and eventual disappearance in the hysteresis was noted as the bulk critical temperature was approached.

These results for the shifted transition are in qualitative agreement with those inferred from adsorption isotherms for Xe in similar VYCOR specimens [2]. In fact the characteristic shape of the step in $N(3\gamma/2\gamma)$ and the associated hysteresis are very similar to the equivalent features observed for adsorption isotherms.

To understand the temperature and pressure dependence of $N(3\gamma/2\gamma)$ it is necessary to identify the processes which influence Ps formation and *o*-Ps annihilation characteristics in capillary confined fluids. Here the total

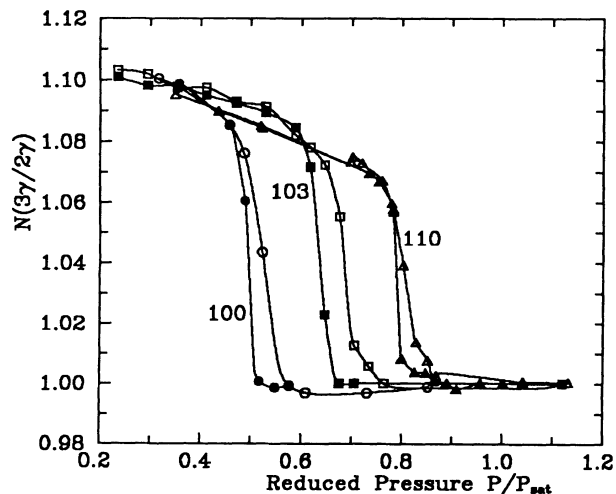


FIG. 3. Ps annihilation parameter $N(3\gamma/2\gamma)$ normalized to the value for filled pores (see Fig. 1) vs reduced pressure for capillary confined nitrogen at 100, 103, and 110 K (open and solid symbols indicate increasing and decreasing pressure, respectively).

positron scattering cross sections reported in the literature [11,12] are useful. The total e^+ scattering cross section for nitrogen gas varies from $\approx 2 \times 10^{-16} \text{ cm}^2$ at 100 eV to a maximum of $\approx 8 \times 10^{-16} \text{ cm}^2$ at $\approx 25 \text{ eV}$ with a minimum of $\approx 3 \times 10^{-16} \text{ cm}^2$ at 5 eV and a value of $\approx 6 \times 10^{-16} \text{ cm}^2$ at 0.25 eV. Cross sections for lower energies have not been reported. Equivalent mean free paths at standard temperature pressure (STP) are $\approx 4 \times 10^3$, $\approx 1 \times 10^3$, $\approx 2.8 \times 10^3$, and $\approx 1.4 \times 10^3 \text{ \AA}$, respectively. Even at 130 K and 35 bars (assuming ideal gas behavior) the mean free path at 25 eV will be $\approx 14 \text{ \AA}$ provided scattering cross sections are density independent.

Since the average pore radius in the VYCOR used for this study was 20 \AA it is evident that nearly all positrons will be moderated in the VYCOR glass matrix. Thus, the Ps which annihilates in the pores is either formed in the glass matrix and migrates to pores or at the pore matrix interface when positrons cross it. In either case the Ps having entered the pore does not reenter the matrix. There is ample evidence for both of these processes in the literature [e.g., [4(c)]]. For our present purposes choosing between them is unnecessary. Since monolayer formation has already occurred above the temperature of the data reported here the pore surface is composed of nitrogen.

Turning to the *o*-Ps annihilation characteristics, which are determined by the quenching processes mentioned in the introduction, we consider the mean free path of Ps in nitrogen gas. A conservative estimate of the collision cross section of Ps gives, at STP, a mean free path of $\approx 2000 \text{ \AA}$ and, again assuming ideal gas behavior, mean free paths in the range $\approx 650 \text{ \AA}$ to $\approx 850 \text{ \AA}$ for temperatures between 100 and 130 K. Now assuming the Ps energy is 0.025 eV results in a Ps speed of $\approx 6.6 \times 10^4 \text{ ms}^{-1}$. Since the Ps mean free path is $\gg 40 \text{ \AA}$, the average empty pore diameter, it is evident that the *o*-Ps pickoff rate will be completely dominated by *o*-Ps-surface collisions. The collision rate will be of order $1 \times 10^{13} \text{ s}^{-1}$ and will obviously depend on the effective pore radius.

Now we have the foundation for a tentative explanation of the shape of the isotherms presented in Fig. 3. The low-pressure linear region results from increased *o*-Ps pickoff at the pore walls as the effective pore radius R_{eff} is reduced via consecutive layer formation at its surface. Such a regime can easily be shown to predict $N(3\gamma/2\gamma) \propto R_{\text{eff}}$ and implies, as is borne out at low pressures in Fig. 3, a temperature-independent value of $N(3\gamma/2\gamma)$. The step in the isotherms results from a gas-liquid phase transition in already partially filled pores or when the pore has been filled to such an extent that the radius R_{eff} is approximately equal to the radius of the self-trapped Ps bubble state which occurs in liquid nitrogen [8]. The second hypothesis would most probably result in a common value of $N(3\gamma/2\gamma)$ immediately prior to the gas-liquid transition which is not borne out in Fig. 3.

Thus, the data presented here suggest that capillary condensation of nitrogen in mesoporous VYCOR occurs via a two-stage process. Initially pore filling occurs via progressive layer formation at the pore surface. This pore filling process is followed by a gas-liquid phase transition at some pressure which is less than the bulk saturated vapor pressure. As the temperature increases the progressive filling process proceeds to higher relative pressures and the pores are more completely filled before condensation occurs. Assuming $N(3\gamma/2\gamma) = 1.1$ for a pore covered by a monolayer and 1.0 for full pores (see Fig. 3), the extent of the progressive pore filling process can be estimated from the current results. Prior to the gas-liquid phase transition the pore filling process results in the formation of approximately 2, 4, and 6 monolayers of nitrogen at 100, 103, and 110 K, respectively. This behavior is consistent with the results of density functional calculations and computer simulation studies of the adsorption isotherms for idealized models of fluids confined in individual pores [2,10]. Finally, provided our hypothesis is correct, the *o*-Ps decay spectrum will have the form $n = n_0 \exp[-(\lambda_p + \lambda_t)t]$, where λ_t and λ_p are the intrinsic (3γ) *o*-Ps and 2γ pickoff annihilation rates, respectively, and n_0 is a normalization constant. The intrinsic 3γ -photon decay rate is constant. The pickoff rate can be written as $\lambda_p = \varepsilon\kappa$ where κ is the *o*-Ps collision rate with the pore surface and ε is the probability of 2γ -photon decay during a collision. Obviously ε will be a property of the pore surface and κ will be inversely proportional R_{eff} . Thus a study of *o*-Ps lifetime spectra, which is currently under way, should provide a direct measure of the variation of effective pore radii with pressure.

The authors would like to thank P. Rice-Evans and D. H. Everett for invaluable discussions during the course of this work. Also we thank D. K. Ross for supplying the

VYCOR samples. Finally we acknowledge the engineering skills of K. J. Dunn and his staff.

-
- [1] S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity* (Academic, New York, 1982).
 - [2] See, e.g., P. C. Ball and R. Evans, *Langmuir* **5**, 714 (1989). This article reproduces the experimental data of S. Nuttall [Ph.D. thesis, University of Bristol, 1974 (unpublished)] for Xe in VYCOR. See also C. G. V. Burgess, D. H. Everett, and S. Nuttall, *Pure Appl. Chem.* **61**, 1845 (1989).
 - [3] J.-C. Li, D. K. Ross, and M. J. Benham, *J. Appl. Crystallogr.* **24**, 794 (1991).
 - [4] For background and reviews see (a) R. N. West, *Positron Studies of Condensed Matter* (Taylor & Francis, London, 1974); (b) *Positron and Positronium Chemistry*, edited by D. M. Schrader and Y. C. Jean (Elsevier Science, New York, 1988); (c) *Positron Scattering in Gases*, edited by J. W. Humberston and M. R. C. McDowell (Plenum, New York, 1984).
 - [5] Corning Reference Data Sheet for Porous VYCOR 7930.
 - [6] *Properties of Materials at Low Temperatures*, edited by V. J. Johnson (Pergamon, New York, 1961).
 - [7] P. Rice-Evans, M. Moussavi-Madani, K. U. Rao, D. T. Britton, and B. P. Cowan, *Phys. Rev. B* **34**, 6117 (1986).
 - [8] A. T. Stewart, C. V. Briscoe, and J. J. Steinbacher, *Can. J. Phys.* **68**, 1362 (1990).
 - [9] T. Kawearatani, Y. Nakayama, and T. Mizogawa, *Phys. Lett.* **108A**, 75 (1985).
 - [10] See, e.g., R. Evans, *J. Phys. Condens. Matter* **2**, 8989 (1990).
 - [11] K. R. Hoffman, M. S. Dababneh, Y.-F. Hsieh, W. E. Kaoppila, V. Pol, J. H. Smart, and T. S. Stein, *Phys. Rev. A* **25**, 1393 (1982).
 - [12] M. Charlton, T. C. Griffith, G. R. Heyland, and G. W. Wright, *J. Phys. B* **16**, 323 (1983).