Bound States of Positrons and Large Molecules

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The lifetime of positrons contained in an electrostatic trap is studied when small quantities of alkanes (i.e., hydrocarbon molecules of the form C_nH_{2n+2}) are added. As n is increased from 4 to 16, the annihilation rate per molecule is found to increase by a factor of 300 and then to level off. These data are interpreted as evidence for the existence of long-lived resonances and bound states of positrons and neutral molecules, and a model of the formation process is discussed.

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In the past two decades, positrons have become available as a laboratory tool to study a wide range of phenomena.[1] We have recently begun experiments to accumulate and store large numbers of positrons in an electrostatic trap.[2] This has allowed us to study the inelastic processes occurring between positrons and molecules. In this Letter, we show that the addition of large organic molecules to the trap increases the annihilation rate of the positrons to the extent that the annihilation process cannot be explained by direct collision phenomena alone, and we infer that long-lived resonances of the positrons and these neutral molecules are formed. A model of the formation process is presented which qualitatively explains the observations including the dependence on molecular size. To our knowledge, these data provide the best evidence to date for the existence of bound states of positrons and neutral molecules.

The experimental arrangement[2] is shown schematically in Fig. 1. Positrons from a ^{22}Na radioactive source are moderated to 2 eV by a single-crystal, tungsten, transmission moderator. They are incident from the right onto the configuration of potentials and neutral-gas pressures shown. The background gas is molecular nitrogen. The gas pressure is adjusted so that, in one transit through the trap, the positrons make inelastic, electronic-excitation or ionizing collisions with the N_2 and are trapped in regions I, II, and III. The potentials are adjusted so that subsequent vibrational excitation of the N_2 traps the positrons, first in regions II and III in about 1 ms (transition B in Fig. 1), and then in region III in less than 1 s (transition B'). The N_2 pressure in region III (the confinement volume) is typically 4.4×10^{-6} Torr, and the base pressure of the vacuum system is less than 3×10^{-8} Torr. The magnetic field in region III is 240 G, and the total number of trapped positrons is always less than 10^4.

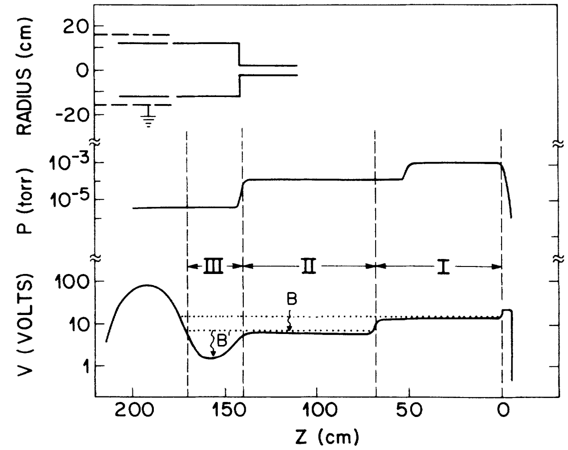

FIG. 1. A schematic diagram of the positron trap showing the electrodes surrounding the confinement region (region III) and the nitrogen-gas pressure and potential profiles along the direction of the axial magnetic field.

After variable fill and storage times, the contents of the trap are dumped onto an arrangement of annular collectors located at $Z=265$ cm in Fig. 1, and the resulting 511-keV γ-ray annihilation radiation is monitored with a NaI detector and pulse-counting electronics. By suitable biasing of the collector plates, either the total number of positrons in the trap or the radial distribution of the positrons can be measured. We have also studied the confinement of electrons in the same geometry.

The characteristic confinement time, τ, of the stored positrons was found to be of the order of 1 s, as compared to confinement times of 100 s for electrons, even when the total number of stored electrons was of the order of 1×10^9, where space-charge effects tend to enhance the radial diffusion. It was the surprisingly short positron confinement time which led to the discovery of the effects central to this Letter.

Measurement of the radial distribution of the positrons indicates that they do not diffuse appreciably on time scales of the order of 1 s but are confined in the central region of the trap. Thus, we conclude that they annihilate before diffusing to the walls. The positron confinement time, τ, is *insensitive* to the N_2 gas pressure, so that the annihilation does not appear to involve the N_2. The key observation is that the positron confinement is extremely sensitive to the history of the vacuum chamber. For example, mild heating of the chamber

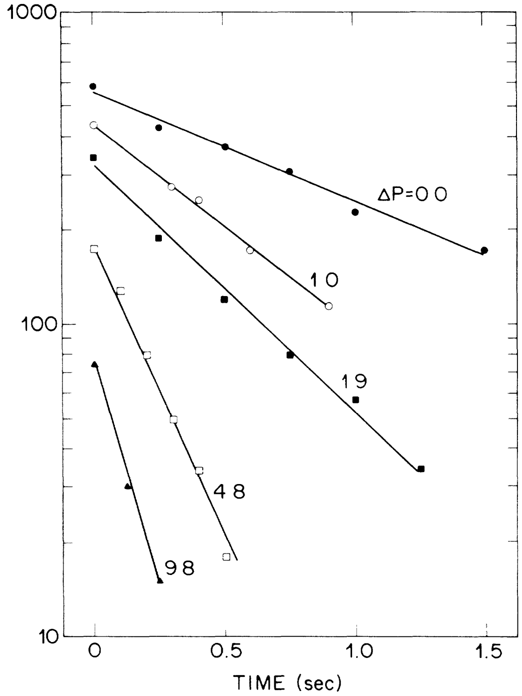

FIG. 2. Positron confinement as a function of storage time when heptane (C_7H_{16}) is introduced into the containment volume (region III) in the presence of 4.4×10^{-6} Torr of N_2 gas. The heptane pressure, ΔP, is in units of 1×10^{-8} Torr.

walls decreases τ, while a liquid-nitrogen-cooled surface near region III increases τ from 1 to 15 s. Thus, we suspected that impurity molecules in the vacuum system were involved.

Previous studies indicate that positron annihilation is well understood for a number of gases, including nitrogen and hydrogen,[3] but is not understood in other gases[3] such as methyl chloride and butane. We introduced specific impurities into the vacuum system to investigate this effect. Water molecules had no effect on τ; but τ was found to be extremely sensitive to the oil from our turbomolecular pumps, to the extent that 1×10^{-9} Torr of oil can explain the observed containment time.

We chose to study the physics of this effect systematically with linear, hydrocarbon molecules (alkanes) of the form C_nH_{2n+2}, for several values of n from 4 to 16. Shown in Fig. 2 are data for the positron confinement as a function of time when small amounts of heptane (C_7H_{16}) are introduced into the vacuum chamber.[4] The number of trapped positrons, $N(t)$, as a function of the storage time, t, can be described by a simple exponential, $N(t)=N(0)\exp(-t/\tau)$, with τ a strong function of the heptane pressure. Similar results were obtained for all of the alkane molecules studied.

In order to analyze the data quantitatively, we assume that the increase in the annihilation rate is proportional to the increase in pressure, ΔP, of the added gas species.

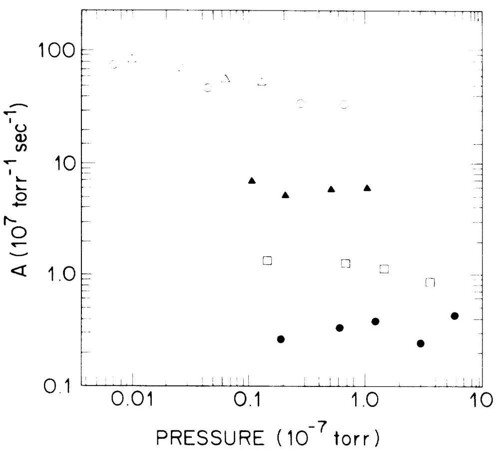

FIG. 3. The annihilation rate per unit pressure, A, of the positrons as a function of the added pressure of alkane molecules: filled circles, butane (C_4H_{10}); open squares, pentane (C_5H_{12}); filled triangles, heptane (C_7H_{16}); open circles, dodecane ($C_{12}H_{26}$); and open triangles, hexadecane ($C_{16}H_{34}$).

Thus,

$$\tau^{-1}=\tau_0^{-1}+A\,\Delta P\,, \tag{1}$$

where τ_0 is the lifetime of the trapped positrons with no alkanes added, and A is a constant. Shown in Fig. 3 are data for several of the alkane molecules. In each case, A is approximately independent of gas pressure, as assumed. The most striking feature of the data is the large increase in A when the size of the alkane molecule is increased.

The annihilation rate, Γ, of positrons in collision with atoms or molecules is historically written in terms of the Dirac annihilation rate for positrons in a free-electron gas[3]; $\Gamma=Z_{\text{eff}}\rho\pi c r_0^2$, where c is the speed of light, r_0 is the classical radius of the electron, ρ is the number density of the gas, and Z_{eff}, which is the effective number of electrons per molecule, takes into account details of the electronic structure. In Fig. 4, we use our measured data for A to infer Z_{eff}/Z as a function of the number of electrons, Z, in the alkane molecule. The data indicate that Z_{eff} for dodecane and hexadecane is approximately 2×10^6. Also shown in Fig. 4 are data for Z_{eff} measured in dense gases.[3] Figure 4 shows an increase in the annihilation rate of over 3 orders of magnitude when the size of the molecule is increased, and it also shows that this effect is not due simply to an increase in the number of electrons.

This large enhancement in the annihilation rate is not likely to be due to an enhancement of the collision cross section, which might be expected to scale with molecular size (i.e., $\sim Z$). Thus, we are led to consider other possibilities, such as a resonance or a bound state of the positron and the molecules. The spin-averaged lifetime of a positronium atom is $\tau_{\text{ps}}\simeq0.5$ ns. Thus, we expect that if

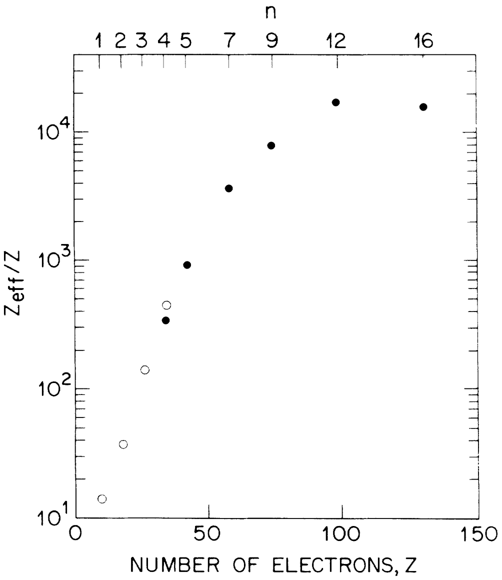

FIG. 4. The quantity Z_{eff}/Z for alkane molecules plotted as a function of the number of electrons, Z, in the molecule; Z_{eff}/Z is the annihilation rate per electron normalized by the Dirac annihilation rate expected in a free-electron gas. Filled circles are the present work; open circles are from Ref. 3. The number of carbon atoms, n, in the alkane molecules studied is indicated by the upper scale.

the resonance lifetime is of the order of τ_{ps}, the positron has unit probability of annihilation. We now compare models of this binding process.

Measurement of the energy spectrum of the trapped positrons with a magnetic energy analyzer indicate that they cool to an energy of 0.7 eV in times less than 0.1 s, which is much smaller than the confinement time, τ, and much larger than the time for annihilation when bound to a molecule. Thus, if binding occurs, it is due to positrons with energies less than 0.7 eV.

Since τ is insensitive to the background N_2 pressure, the binding appears to be due to a two-body process. Such processes have been discussed in the context of electrons binding to neutral molecules,[5] and we are led to a similar picture. The positrons have enough energy to directly excite low-energy vibrational modes in the large molecule, but are not likely to excite electronic excitations in the molecule or to dissociate it. If we *assume* that the positron has an energy affinity, ϵ_A, for the molecule, then the incident positron energy plus some fraction or all of ϵ_A can be used to excite vibrational modes, in which case the positron will be attached to the molecule.

A reasonable explanation of the plateau in Z_{eff}/Z shown in Fig. 4, when Z is increased beyond $Z \simeq 74$, is that, with increasing size, the lifetime τ_m, of the complex has become comparable to the annihilation time ($\tau_m \simeq \tau_{\mathrm{ps}}$). If we make this assumption, then we find a cross section of $\sigma \simeq 3\times10^{-16}$ cm^2 for the binding of the positron and a molecule with $Z=74$ (i.e., nonane, C_9H_{20}). Our measurements of the cooling of the positrons by N_2 indicate that the inelastic, e^+-N_2 vibrational cross section is of the order of 0.5×10^{-17} cm^2. Thus, a value of 3×10^{-16} cm^2 for C_9H_{20} does not seem unreasonable.

With use of detailed-balance arguments, an expression for τ_m has been derived for the case of electrons bound to molecules.[5] It can be written in terms of the electron affinity, ϵ_A, the incident electron energy, ϵ_i, the number, l, of vibrational modes of the molecule, and their total zero-point vibrational energy, ϵ_z. In particular,

$$\tau_m^{-1} = (m_e/\pi^2\hbar^3)\epsilon_i^{1/2}\tilde{\epsilon}_z^{3/2}[\tilde{\epsilon}_z/(\epsilon_A+\tilde{\epsilon}_z)]^l\sigma(\epsilon_i,\epsilon_z)\,, \quad (2)$$

where $I(\epsilon_i,\epsilon_z)$ is a definite integral[5]; $\tilde{\epsilon}_z = b\epsilon_z$, with b a correction factor differing from unity by a few tens of percent[6]; and $\sigma(\epsilon_i)$ is the excitation cross section discussed above.

There are two features of Fig. 4 which can be compared with Eq. (2) to yield estimates of the positron affinity ϵ_A—the plateau beginning at $Z=74$ and the slope of $\ln(\tau_m)$ vs Z at small Z. Using Eq. (2) for our positron data at $Z=74$ with $\epsilon_i=0.3$ eV, and assuming $\sigma(\epsilon_i)=3\times10^{-16}$ cm^2, $l=81$ (corresponding to $Z=74$), and $\tau_m=0.5\times10^{-9}$ s, we find $\epsilon_A/\tilde{\epsilon}_z=0.05$. We now compare the slope of the curve in Fig. 4 at small values of Z to $d\ln(\tau_m)/dl$. Changes in Z are linearly proportional to changes in l (i.e., $\Delta l = \frac{9}{8}\Delta Z$). Thus, the dominant dependence of $\ln(\tau_m)$ on Z will come from the factor $[\tilde{\epsilon}_z/(\epsilon_A+\tilde{\epsilon}_z)]^l$ in Eq. (2), even if $\sigma(\epsilon_i)$ and $I(\epsilon_i\epsilon_z)$ have some l dependence. The observed linear slope in Fig. 4 will occur only if $\epsilon_A \propto \tilde{\epsilon}_z$, indicating that ϵ_A increases linearly with the size of the alkane molecule. On comparing the data to Eq. (2), we find $\epsilon_A/\tilde{\epsilon}_z=0.14$. The two estimates of $\epsilon_A/\tilde{\epsilon}_z$ differ by a factor of 3. For $Z=74$, we estimate $\epsilon_z \simeq 13$ eV and assume $b \simeq 0.8$ (Ref. 6) to find that ϵ_A is in the range $0.5 \lesssim \epsilon_A \lesssim 1.5$ eV.

The sign of ϵ_A is such that the positrons can form bound states with the molecules. However, energy is conserved in the two-body collisions studied here. Thus, the positrons are not bound, since this would require subsequent collisions to drain off the energy. Instead, they form resonances in which the positrons annihilate with increasing probability as the lifetime of the resonance increases. The data are consistent with the model presented here; however, it is clear that further work is necessary. In particular, it would be useful to have calculations of both the magnitude of ϵ_A and its dependence on molecular size for the case of positrons bound to alkane molecules.

In this Letter, we have presented a study of the lifetime of positrons in the presence of large alkane molecules. We interpret these data to imply the existence of long-lived resonances and bound states of positrons and neutral molecules. These results raise a number of interesting questions, such as prediction of the positron-molecule affinity, ϵ_A. These bound states might also be expected to have implications for other physical situations, and appear to open up the possibility of using positrons to study aspects of molecular physics and small insulating clusters. For example, annihilation in such bound states might be used to produce positive ions in cases where electron impact ionization would break up a fragile molecular species.[7]

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[1] See, for example, articles in *Positron Studies of Solids, Surfaces and Atoms,* edited by A. P. Mills, Jr., W. S. Crane, and K. F. Canter (World Scientific, Singapore, 1986).

[2] C. M. Surko, M. Leventhal, W. S. Crane, A. Passner, F. J. Wysocki, T. J. Murphy, J. Strachan, and W. L. Rowan, Rev. Sci. Instrum. **57**, 1862 (1986); F. J. Wysocki, M. Leventhal, A. Passner, and C. M. Surko, in Proceedings of Antimatter '87, Karlsruhe, West Germany, edited by A. Wolf and H. Poth, Hyperfine Int. (to be published).

[3] G. R. Heyland, M. Charlton, T. C. Griffith, and G. L. Wright, Can. J. Phys. **60**, 503 (1982). This study of positron annihilation in dense gases reports annihilation rates per molecule for butane which are in good agreement with our measurements. The authors suggest that the large rates which are observed might be due to bound-state formation, which is the conclusion of this Letter.

[4] Pressures were measured with a Varian, Bayard-Alpert gauge. Calibrations for alkane molecules were taken from J. E. Bartness and R. M. Georgiadias, Vacuum **33**, 149 (1983).

[5] L. G. Christophorou, A. Hadjiantoniou, and J. G. Carter, J. Chem. Soc. Faraday Trans. 2 **69**, 1713 (1973); L. G. Christophorou, D. L. McCorkle, and A. A. Christodoulides, *Electron-Molecule Interactions and Their Applications* (Academic, New York, 1984), Vol. 1, pp. 478–618.

[6] G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys. **38**, 2466 (1963).

[7] See D. Schrader, D. L. Donohue, G. L. Glish, S. A. McLuckey, L. D. Hewlett, Jr., H. S. McKown, and S. Pendyala, in Proceedings of the Eighth International Conference on Positron Annihilation, Gent, Belgium, 1988 (World Scientific, Singapore, to be published).