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### Ion production by positron-molecule resonances

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We have recently discovered that positrons form long-lived resonances with large molecules. We present a study of the positive ions that are produced when the positrons annihilate with an electron in such a resonance for the case of alkane molecules ( $C_nH_{2n+2}$ ). This method of ion production is qualitatively different than those conventionally used and may be useful in the chemical analysis of unknown molecular species by mass spectrometry.

In the past two decades, study of the interaction of positrons with ordinary matter has led to new insights into the nature of solids, surfaces, atoms, and molecules.<sup>1</sup> We have developed an electrostatic trapping scheme to efficiently accumulate and store large numbers of positrons.<sup>2</sup> Among other uses, this allows us to study the interaction of positrons with atoms and molecules. We have recently discovered that the positrons form long-lived resonances with large, neutral molecules.<sup>3</sup> This discovery leads us to the deduction that a positive ion will be formed when the positron annihilates with an electron on the molecule. It has been pointed out that this would be a qualitatively different way of producing positive ions, and might have potential applications in chemical analysis using mass spectrometry.<sup>4</sup> For example, this mechanism for ion formation might be a more gentle way to form ions from fragile molecular species than conventional techniques such as electron-impact ionization. In this paper, we present time-of-flight spectra of the positive ions formed in such resonances for the case of alkane molecules ( $C_nH_{2n+2}$ ).

The positron trap, which has been described elsewhere,<sup>2,3</sup> is shown schematically in Fig. 1. Positrons from a radioactive  $^{22}\text{Na}$  source are moderated to 2 eV by a single-crystal tungsten moderator. They are then guided by an axial magnetic field to a set of electrodes with three different regions of electrical potential and  $\text{N}_2$  gas pressure, labeled regions I–III in Fig. 1. The pressures are adjusted so that the positrons make, on average, one or more electronic excitation or ionization collisions in region I in one transit through the trap. They are confined to the sum of regions I, II, and III. Subsequent vibrational excitations of the  $\text{N}_2$  trap them in regions II and III and then finally in region III. The potentials on the electrodes are adjusted so that positronium atom formation, which has an energy threshold of 8.8 eV in  $\text{N}_2$ , can only occur in re-

gion I, thereby avoiding this loss process for the positrons in the final two stages, regions II and III.

At an operating  $\text{N}_2$  pressure of  $1.5 \times 10^{-6}$  Torr in region III, the positrons are trapped in this region after remaining about 20 ms in regions II plus III. They are found to cool to average energies of 1 eV, after about 40 ms in region III, and then to cool to room temperature with a characteristic,  $1/e$  time of 0.6 s. The resulting room-temperature positron gas is confined by the magnet-

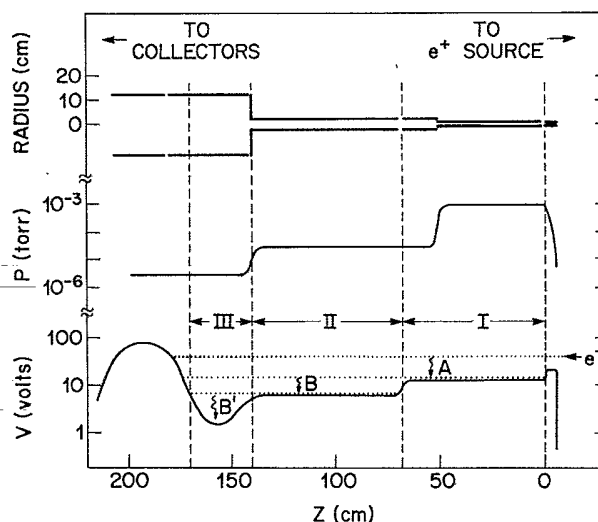


FIG. 1. Shown is a schematic of the three-stage positron trap, including the electrode structure, a typical profile of the  $\text{N}_2$  gas pressure, and the applied electrostatic potentials. There is an axial magnetic field of 860 G in the  $Z$  direction. The positrons typically make three or more inelastic collisions with the  $\text{N}_2$  (indicated by A, B, and B') to become trapped in region III in times of the order of 20 ms after entering the trap.

ic field and the applied electrostatic potentials to an elliptical volume of the order of 3 cm in diameter by 2.4 cm long. When additional pumping is provided by cold surfaces to eliminate spurious impurities, the lifetime of the positrons is 60 s for an  $N_2$  pressure of  $1.5 \times 10^{-6}$  Torr in region III.<sup>3</sup> In this case, the lifetime is limited by direct annihilation with the  $N_2$ . However, when large molecules, such as alkanes ( $C_nH_{2n+2}$ ) are added, the positron lifetime drops precipitously, particularly when  $n \geq 9$ .<sup>3</sup> For example,  $1 \times 10^{-10}$  Torr of dodecane ( $C_{12}H_{26}$ ) limits the positron lifetime to 1 s due to annihilation in positron-molecule resonances. The existence of these resonances greatly enhances the probability that the positron will annihilate with an electron in the molecule.<sup>3</sup> For  $C_{12}H_{26}$ , the probability of annihilation is of the order of  $2 \times 10^4$  times greater than that expected for the conventional process of "direct annihilation," in which a positron annihilates during an elastic collision with the molecule.

In order to study the ions formed by such positron-molecule resonances, we installed a two-stage channel-plate, electron multiplier 100 cm away from the center of region III (i.e., at  $Z = 260$  cm in Fig. 1). The electrode surrounding region III was biased at 5 V to accelerate ions toward the channel plate. After suitable fill and storage times, the potential barrier located near 195 cm in Fig. 1 is lowered, and the contents of the trap are dumped onto the channel plate. The channel plate is biased at  $-2400$  V, providing near-unity detection efficiency for ions with masses in the range studied (i.e., 10–150 amu). When the ion signal is measured as a function of time delay after the trap is dumped, we have a simple, time-of-flight mass spectrometer.

Our studies indicate that many molecular species form long-lived positron-molecule resonances. We have chosen to study the ions formed when alkane molecules are added to the trap, since we have previously documented in detail the resonances of positrons with this particular molecular species.<sup>3</sup> Shown in Fig. 2 is the channel-plate signal as a function of time  $\tau$ , after the contents of the trap are dumped when butane ( $C_4H_{10}$ ) is added to region III.<sup>5</sup> The signal at zero storage time, which is typical of that when no butane is added, shows a prompt peak at  $t = 0$ , corresponding to the trapped positrons, and a peak at 185  $\mu$ s which corresponds to  $N_2^+$ . The  $N_2^+$  ions are formed in region I, when the positrons ionize the  $N_2$ , and this signal decreases monotonically as a function of storage time. Based on the simplest calculation using the applied potentials, the expected arrival time of the  $N_2^+$  would be 170  $\mu$ s, which is 9% lower than that measured. When  $CO_2$  was introduced into the system, the expected arrival time was also 9% lower, and so the expected arrival times for all ions were scaled by this factor in order to identify the ion species detected.

In addition to the  $e^+$  and  $N_2^+$  signals, three other ion peaks are evident in Fig. 2. Our identification of these signals is indicated above the figure. The decay time of the ion signals is strongly dependent on the applied magnetic field. This is consistent with estimates of the radial diffusion of these species out of the region where they are detected by the channel plate. In contrast, direct measurements of the radial distribution of the  $e^+$  show that

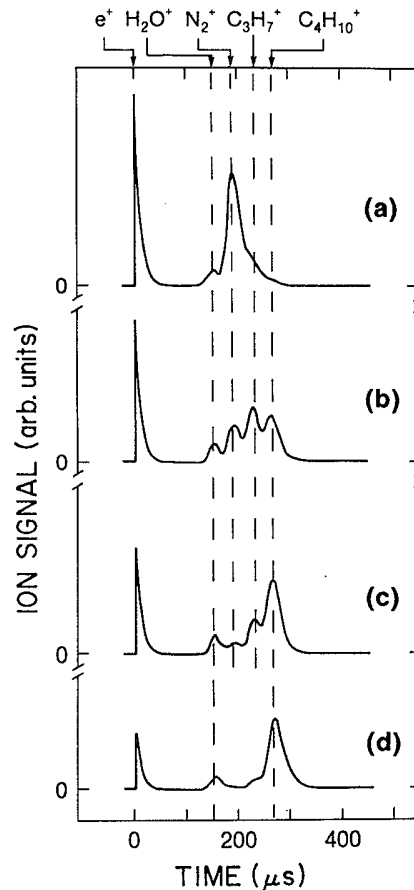


FIG. 2. Time-of-flight spectra of the ions observed when the trap positron is dumped, for the case where butane is added to region III. The traces correspond to storage times of (a) 0 s, (b) 0.5 s, (c) 1 s, and (d) 2 s. The filling time was 0.5 s, the  $N_2$  pressure in region III was  $0.5 \times 10^{-7}$  Torr, and the butane pressure was  $2.5 \times 10^{-7}$  Torr. The identification of the peaks and their expected positions are indicated.

they do not diffuse appreciably on the time scale of the experiment. This is consistent with the estimates of the cross-field diffusion expected for the positrons.<sup>2</sup>

After about 1 s, the dominant ion peak occurs at 265  $\mu$ s and corresponds to butane ions  $C_4H_{10}^+$ . The time dependence of this signal and the  $e^+$  are shown in Fig. 3. We have previously shown that the annihilation rate of the positrons is directly proportional to the  $C_4H_{10}$  density.<sup>3</sup> Thus, we would expect that the time dependence of the  $C_4H_{10}^+$  could be described by the solution of the rate equations for the  $e^+$  and  $C_4H_{10}^+$ , assuming that the population of each decays exponentially in time, with the first feeding the second (i.e., "parent-daughter decay" common in nuclear physics).<sup>6</sup> If we assume that the number of positrons as a function of time is  $N_p(t) = N_0 \exp(-At)$  and that the number of butane ions  $N_b$  are lost from the field of view of the detector at a rate  $dN_b/dt = -BN_b$ , the time dependence of  $N_b$  is given by<sup>6</sup>

$$N_b(t) = [N_0 A / (B - A)] [\exp(-At) - \exp(-Bt)]. \quad (1)$$

The solid curve in Fig. 3 is the fit of an exponential to  $N_p(t)$ , which yields  $A = 0.56$  s. In order to compare the

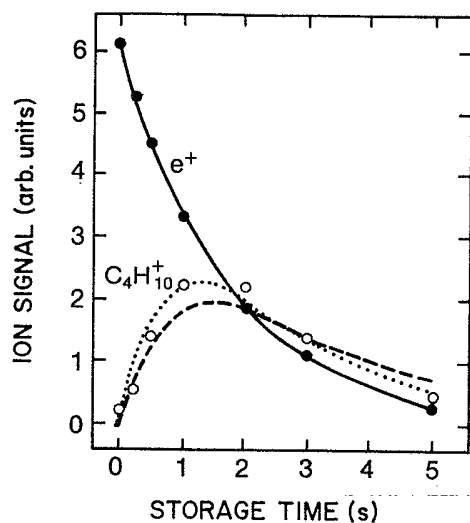


FIG. 3. The peak amplitudes of the  $e^+$  (filled circles) and  $C_4H_{10}^+$  ion (open circles) signals are plotted as a function of storage time, for the data shown in Fig. 2. The dashed and dotted curves are solutions of a rate-equation model of the butane ion production by the annihilating positrons. See text for details.

butane ion data with the solutions of Eq. (1), we must take into account the larger width of the ion peaks as compared with that of the positron signal (approximately a factor of 3) and the difference in detection efficiency  $\eta$  of the butane ions relative to that of the positrons. The dotted curve in Fig. 3 is the best fit to Eq. (1) and corresponds to  $\eta=4.5$  and  $B=1.06$ . For comparison, the dashed curve is a solution for  $\eta=3$  and yields  $B=0.69$ . Our estimates of  $\eta$  indicate that  $2 \lesssim \eta \lesssim 3$ . Both the shape and the absolute amplitude of the  $C_4H_{10}^+$  signal are reasonably well represented by Eq. (1). Thus, this analysis supports the picture that the positrons annihilate with the neutral butane molecules leaving  $C_4H_{10}^+$  ions behind.

For the analyses described above, the filling time of 0.5 s is significantly long so that it should be taken into account. However, the butane ion data are best fit ignoring this effect (i.e., the butane ion signal is very small at the end of the fill cycle). While we do not understand this in detail, it is likely that the positrons take an appreciable fraction of filling time to cool down to an energy which is low enough so that they can bind to the butane.<sup>3</sup>

The two other identifiable peaks in Fig. 2 appear to be  $H_2O^+$  (150  $\mu s$ ) and  $C_3H_7^+$  (235  $\mu s$ ).<sup>7</sup> Water is a likely impurity in our vacuum system and appears to play little or no role in the dynamics of the other species. The rise time and the amplitude of the  $C_3H_7^+$  signal are consistent with it being generated by charge exchange between the  $N_2^+$  and the butane, producing  $C_3H_7^+$  and other products. We have carried out an analysis of the  $N_2^+$ - $C_3H_7^+$  data similar to that described above for the  $e^+$ - $C_4H_{10}^+$  data which supports this hypothesis.

Shown in Fig. 4 are data for the ions produced when heptane ( $C_7H_{16}$ ) is added to region III. In this case, heptane ions are observed, but never as the dominant peak which appears to correspond to  $C_4H_9^+$ .<sup>6</sup> The previously

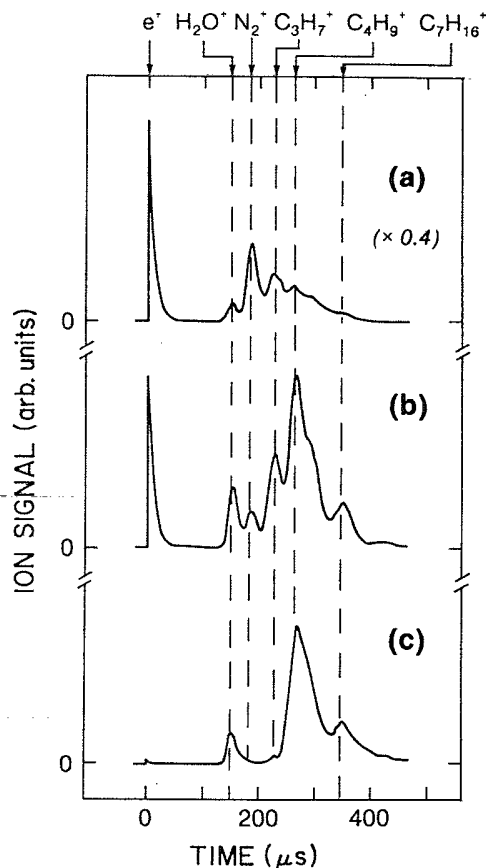


FIG. 4. Time-of-flight spectra of the ions observed when the trap is dumped, for the case where heptane ( $C_7H_{16}$ ) is added to the trap: The storage times are (a) 0.5 s, (b) 2 s, and (c) 4 s. The filling time was 0.2 s in (a) and 1 s in (b) and (c). The identification of the peaks and their expected positions are indicated.

observed  $N_2^+$ ,  $H_2O^+$ , and  $C_3H_7^+$  peaks are also evident. The  $C_4H_9^+$  and  $C_7H_{16}^+$  signals are approximately proportional to each other. They increase at early times as the positrons disappear in a manner similar to that described above for  $C_4H_{10}^+$ . These data indicate that the positrons can breakup large molecules into fragments. The details of this process remain to be studied.

The results presented here show that positrons can be used to form positive ions from large neutral molecules. Because of the formation of long-lived  $e^+$ -molecule resonances, the cross sections for these processes are much larger than previously anticipated. Since this ion formation process is qualitatively different than conventional techniques for forming positive ions, it may be useful in obtaining additional information about unknown molecular species when these molecules are studied using mass spectrometry. It is also possible that more detailed studies of the specific ions formed from a given molecule after positron annihilation may give insight into the nature of the  $e^+$ -molecule resonances themselves.

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<sup>1</sup>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), and in *Positron Annihilation Studies in Fluids*, edited by S. C. Sharma (World Scientific, Singapore, 1988).

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<sup>3</sup>C. M. Surko, A. Passner, M. Leventhal, and F. J. Wysocki,

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<sup>4</sup>D. M. Schrader, *Can. J. Phys.* **60**, 574 (1982); D. M. Schrader, in *Proceedings of the Eighth International Conference on Positron Annihilation, Gent, Belgium, 1988*, edited by D. Dorikens-Vanparet, M. Dorikens, and D. Segers (World Scientific, Singapore, in press), D. L. Donohue, G. L. Glish, S. A. McLuckey, L. D. Hewlett, Jr., H. S. McKown, and S. Pendyala, *ibid.*

<sup>5</sup>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).

<sup>6</sup>See, for example, W. R. Leo, *Techniques for Nuclear and Particle Physics Experiments* (Springer-Verlag, New York, 1987).

<sup>7</sup>The data are not of sufficient resolution to determine the precise numbers of hydrogen atoms in these ions, so the numbers of hydrogen were chosen based on what are likely to be stable ions [K. Raghavachari (private communication)].