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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.[1] We have developed an electrostatic trapping scheme to efficiently accumulate and store large numbers of positrons.[2] 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.[3] 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.[4] 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,[2,3] is shown schematically in Fig. 1. Positrons from a radioactive ^{22}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 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 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 N_2, can only occur in region I, thereby avoiding this loss process for the positrons in the final two stages, regions II and III.

At an operating N_2 pressure of 1.5×10^{-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-
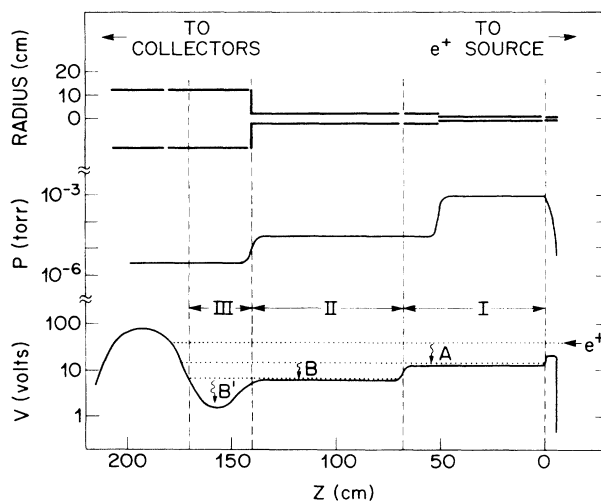

FIG. 1. Shown is a schematic of the three-stage positron trap, including the electrode structure, a typical profile of the N_2 gas pressure, and the applied electrostatic potentials. There is an axial magnetic field of 860 G in the Z direction. The positrons typically make three or more inelastic collisions with the 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 ellip-
tical volume of the order of 3 cm in diameter by 2.4 cm
long. When additional pumping is provided by cold sur-
faces to eliminate spurious impurities, the lifetime of the
positrons is 60 s for an N_2 pressure of 1.5×10^{-6} Torr in
region III.[3] 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 life-
time drops precipitously, particularly when $n \geq 9$.[3] For
example, 1×10^{-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 an-
nihilate with an electron in the molecule.[3] For $C_{12}H_{26}$,
the probability of annihilation is of the order of 2×10^4
times greater than that expected for the conventional pro-
cess of "direct annihilation," in which a positron annihi-
lates 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.[3] Shown in Fig. 2 is the channel-plate signal as a
function of time τ, after the contents of the trap are
dumped when butane (C_4H_{10}) is added to region III.[5]
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
μs which corresponds to N_2^+. The N_2^+ ions are formed
in region I, when the positrons ionize the N_2, and this sig-
nal decreases monotonically as a function of storage time.
Based on the simplest calculation using the applied poten-
tials, the expected arrival time of the N_2^+ would be 170
μs, 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 sig-
nals 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 dif-
fusion of these species out of the region where they are
detected by the channel plate. In contrast, direct mea-
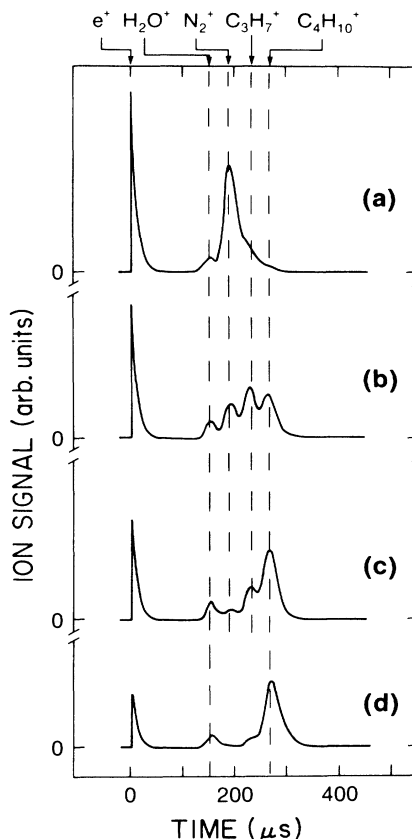surements of the radial distribution of the e^+ show that

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 pres-
sure in region III was 0.5×10^{-7} Torr, and the butane pressure
was 2.5×10^{-7} Torr. The identification of the peaks and their
expected positions are indicated.

they do not diffuse appreciably on the time scale of the ex-
periment. This is consistent with the estimates of the
cross-field diffusion expected for the positrons.[2]

After about 1 s, the dominant ion peak occurs at 265 μs
and corresponds to butane ions $C_4H_{10}^+$. The time depen-
dence 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.[3]
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 pop-
ulation of each decays exponentially in time, with the first
feeding the second (i.e., " parent-daughter decay" com-
mon in nuclear physics).[6] 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[6]

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

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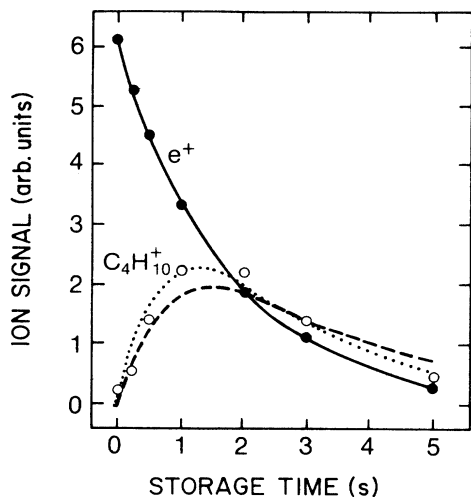$N_p(t)$, which yields $A = 0.56$ s. In order to compare the

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.

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.

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 η 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 η 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.[3]

The two other identifiable peaks in Fig. 2 appear to be H_2O^+ (150 μs) and $C_3H_7^+$ (235 μs).[7] 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 app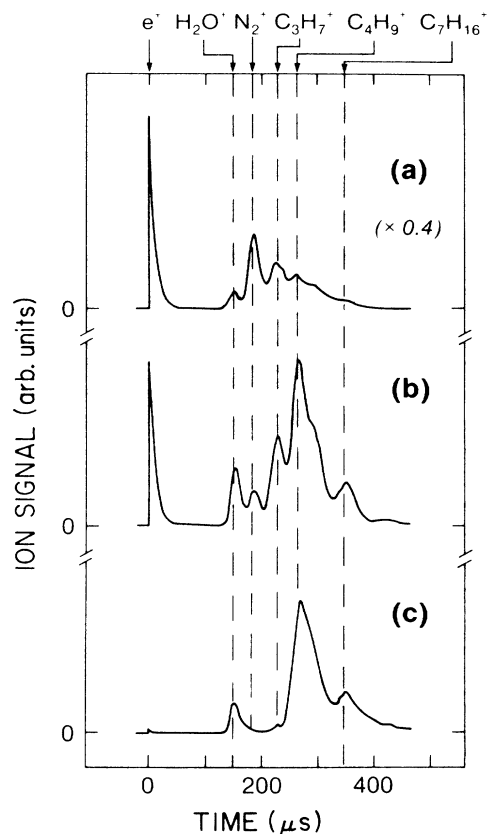ears to correspond to $C_4H_9^+$.[6] The previously observed N_2^+, H_2O^+, and $C_3H_7^+$ peaks are also evident. The $C_4H_9^+$ and $C_7H_{16}^+$ signals are approximately proportional to each other. They increase at early times as the positrons disappear in a manner similar to that described above 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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[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), and in *Positron Annihilation Studies in Fluids,* edited by S. C. Sharma (World Scientific, Singapore, 1988).

[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 1987 Karlsruhe, Germany,* edited by A. Wolf and H. Poth [Hyperfine Int. (to be published)]; C. M. Surko, M. Leventhal, A. Passner, and F. J. Wysocki, in *Non-Neutral Plasmas,* edited by C. W. Roberson and C. F. Driscoll, AIP Conference Proceedings No. 175 (American Institute of Physics, New York, 1988), p. 75.

[3]C. M. Surko, A. Passner, M. Leventhal, and F. J. Wysocki, Phys. Rev. Lett. **61**, 1831 (1988).

[4]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.*

[5]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).

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

[7]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)].