

## Annihilation of Positrons on Organic Molecules

T. J. Murphy<sup>(a)</sup> and C. M. Surko

*Physics Department, University of California, San Diego, La Jolla, California 92093*

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The lifetime of positrons confined in a Penning trap is studied in the presence of a variety of chemical species. The large observed annihilation rates of the positrons on these molecules provide evidence that positron-molecule attachment is a general phenomenon, and distinct chemical trends are identified. For example, the annihilation rate on fluorocarbons is as much as 3 orders of magnitude smaller than that for the analogous hydrocarbons. An empirical scaling of the dependence of the annihilation rate on molecular ionization potential is identified.

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Many aspects of the interaction of positrons with ordinary matter are understood in detail. One exception is the interaction of positrons with molecules below the threshold for positronium atom formation. While the annihilation of positrons on small atoms and molecules, such as helium, neon, molecular hydrogen, and molecular nitrogen, can be understood in terms of simple collisions [1], there is evidence that such a picture does not hold for larger molecules such as alkanes (i.e.,  $C_nH_{2n+2}$ , for  $n=1,2,\dots$ ) [1-4]. For these molecules, the annihilation rate is large compared to that which one would expect from simple, two-body collisions. It has been conjectured [2,3] that this is due to the attachment of the positron to the molecule (i.e., in long-lived, positron-molecule resonances); however, at present, we know of no adequate theoretical model to describe this process.

There is evidence that this phenomenon depends on the specific molecular species [1-3]. In this Letter, we describe a systematic study of positron annihilation in the presence of a variety of chemical species, including alkanes, substituted alkanes (such as perfluorocarbons), aromatics, and fluorine-substituted aromatics in the isolated environment of a Penning trap. Our results indicate that there is a continuous progression to higher annihilation rate with increasing molecular size, but that distinct chemical trends are also present. For example, perfluorocarbons have a much smaller annihilation rate than the analogous hydrocarbons, and the benzene molecule has a very small annihilation rate when compared to related chemical species. Finally, we identify a phenomenological scaling of the logarithm of the annihilation rate with the inverse of the difference between the ionization potential of the atom or molecule and the binding energy of a positronium atom.

The experiments were performed with room-temperature positrons confined in a Penning trap in a manner similar to previous measurements of the annihilation rate of positrons on xenon [5]. Substances which exist as liquids or solids at atmospheric pressure may be added to the trap in vapor form in quantities sufficient to measurably affect the annihilation rate in the trap. The use of low-pressure gases ensures that we are studying a binary

process involving just one positron and one molecule. The positron temperature in the trap can be directly measured, and, for the data presented here, the positrons are at room temperature. For the molecules studied, this is from 0.67 to 18 eV below the positron energy required for positronium atom formation, which eliminates this process as a channel for positron annihilation.

The positron trap consists of three stages, each operating at a different pressure of  $N_2$  gas. The operation of the trap is described in detail in Ref. [5]. Positrons from a  $^{22}Na$  source are slowed to a few electronvolts using a tungsten transmission moderator, and they are then guided into the trap by a solenoidal magnetic field. The pressure of nitrogen gas in the first stage is adjusted so that, on average, the positrons experience one inelastic collision upon traversing the length of this stage, and they are then trapped within the electrode structure. Subsequent electronic excitation collisions result in the positrons becoming confined to the second and third stages and finally to the third stage in a time of the order of 30 ms. The  $N_2$  gas pressure in the third stage is  $2 \times 10^{-6}$  torr. The positrons cool to room temperature (i.e., the temperature of the nitrogen gas) in approximately 2 s, in a region where the total gas pressure is kept sufficiently low that subsequent radial diffusion across the magnetic field is negligible.

Various gases and vapors may be added directly to the third stage of the trap. The molecules used in these studies were the highest purity commercially available. The liquids were degassed prior to use by repeated cycles of freezing and thawing under vacuum.

The annihilation rate of the positrons is determined by accumulating positrons for a fixed amount of time (filling) and then waiting a variable amount of time while the positrons annihilate (storing) before dumping the remaining positrons onto a metal plate and measuring the characteristic 511-keV annihilation radiation. This radiation is measured using a NaI(Tl) scintillator, with the amplitude of the light pulse proportional to the number of positrons remaining. Typical data for  $C_8F_{18}$  are shown in Fig. 1.

For a binary process, the annihilation rate is a linear

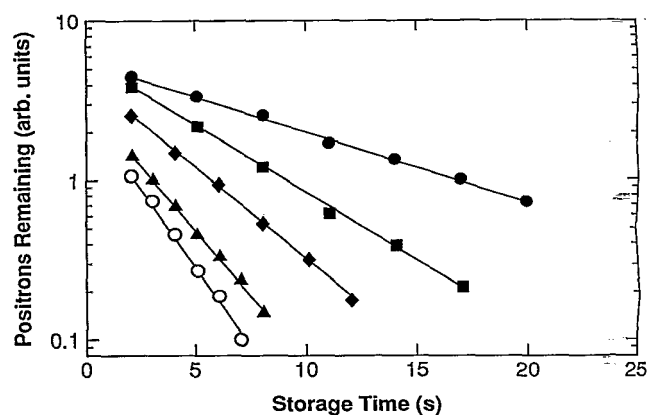


FIG. 1. The number of positrons remaining in the trap as a function of storage time for a 5-s fill when  $C_8F_{18}$  is added to the trap at pressures of, ●, 0.00; ■, 0.36; ◆, 0.65; ▲, 1.04; and ○, 1.25  $\mu$ torr. The solid lines are least-squares fits to the data.

function of molecular density and is given by  $\Gamma = \Gamma_0 + \gamma_1 P_{N_2} + \gamma_x P_x$ , where  $\gamma_1$  and  $\gamma_x$  are constants proportional to the annihilation rate per molecule of nitrogen and the molecule under study, respectively,  $P_{N_2}$  and  $P_x$  are the pressures of these gases, and  $\Gamma_0$  is the annihilation rate on other large molecules present as contaminants in the trap. For all of the molecules studied,  $\Gamma$  is found to be linear in  $P_x$  as described by the above equation.

TABLE I. Measured values of  $Z_{\text{eff}}$  for substituted alkanes, hexenes, aromatics, and aromatic perfluorocarbons.

Molecule	Formula	Z	$Z_{\text{eff}}$
Carbon tetrafluoride	CF <sub>4</sub>	42	54.4
Perfluoropropane	C <sub>3</sub> F <sub>8</sub>	90	151.5
Perfluorohexane	C <sub>6</sub> F <sub>14</sub>	162	535
Octadecafluorooctane	C <sub>8</sub> F <sub>18</sub>	210	1064
Carbon tetrachloride	CCl <sub>4</sub>	74	9530
Hexachloroethane	C <sub>2</sub> Cl <sub>6</sub>	114	68600
Carbon tetrabromide	CBr <sub>4</sub>	146	39800
Hexane	C <sub>6</sub> H <sub>14</sub>	50	98000
1-hexene	C <sub>6</sub> H <sub>12</sub>	48	185000
trans 3-hexene	C <sub>6</sub> H <sub>12</sub>	48	196000
1,3-hexadiene	C <sub>6</sub> H <sub>10</sub>	46	389000
cis 2, trans 4-hexadiene	C <sub>6</sub> H <sub>10</sub>	46	413000
trans 2, trans 4-hexadiene	C <sub>6</sub> H <sub>10</sub>	46	388000
1,3,5-hexatriene	C <sub>6</sub> H <sub>8</sub>	44	414000
Benzene	C <sub>6</sub> H <sub>6</sub>	42	18400
Toluene	C <sub>7</sub> H <sub>8</sub>	50	155000
Naphthalene	C <sub>10</sub> H <sub>8</sub>	68	494000
Anthracene	C <sub>14</sub> H <sub>10</sub>	94	4330000
Decahydronaphthalene <sup>a</sup>	C <sub>10</sub> H <sub>18</sub>	78	389000
Hexafluorobenzene	C <sub>6</sub> F <sub>6</sub>	90	1200
Octafluorotoluene	C <sub>7</sub> F <sub>8</sub>	114	1240
Octafluoronaphthalene	C <sub>10</sub> F <sub>8</sub>	132	3080

<sup>a</sup>Reference [3].

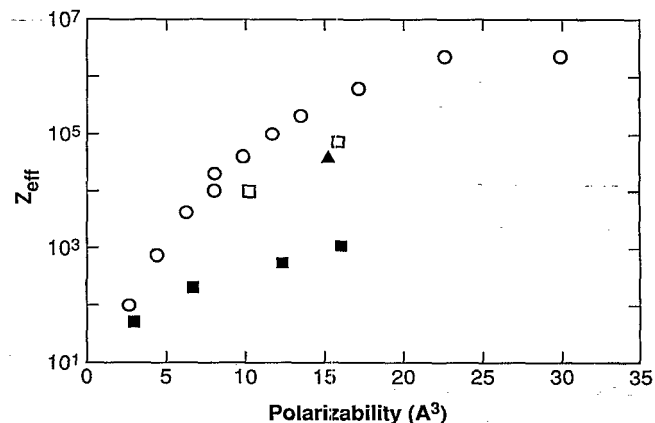


FIG. 2. The annihilation rate per molecule, in units of  $Z_{\text{eff}}$ , as a function of molecular polarizability for, ○, alkanes (from Refs. [1,3]) and the substituted alkanes, ■,  $C_nF_{2n+2}$ ; □,  $C_nCl_{2n+2}$ ; and ▲,  $C_nBr_{2n+2}$  (from Table I).

For small atoms and molecules, annihilation rates are usually expressed relative to the Dirac annihilation rate of positrons in a gas of uncorrelated electrons [1],

$$\Gamma_x = \gamma_x P_x = \pi r_0^2 c n_x Z_{\text{eff}}, \quad (1)$$

where  $n_x$  is the number density of atoms or molecules,  $r_0$  is the classical radius of the electron, and  $c$  is the speed of light [3]. For small molecules,  $Z_{\text{eff}}$  is interpreted as the effective number of electrons taking part in the annihilation process. For large molecules,  $Z_{\text{eff}} \gg Z$  [1-3], where  $Z$  is the total ionic charge on the molecule, so that the idea of the positron interacting with the molecule in isolated collisions of short duration is no longer plausible. In this Letter, we plot the data in terms of  $Z_{\text{eff}}$ , which represents the annihilation rate per molecule. For  $Z_{\text{eff}} \gg Z$ , one interpretation of the ratio  $Z_{\text{eff}}/Z$  is that it is roughly the average duration of a positron-molecule resonance relative to the duration of a simple, elastic collision.

At large distances, the interaction between a positron and a molecule is proportional to the molecular polarizability, and  $Z_{\text{eff}}$  is conventionally plotted with this as a parameter. However, previous data for  $\Gamma_x$  suggest that there are large differences between different chemical species when molecules with similar molecular polarizabilities are considered [1,3]. For example, SF<sub>6</sub> has a  $Z_{\text{eff}}$  of 90 as compared with ethane (C<sub>2</sub>H<sub>6</sub>) with  $Z_{\text{eff}}$  of 700 [1], even though ethane has fewer electrons and a similar molecular polarizability [6]. We have now studied these effects systematically, and results for  $Z_{\text{eff}}$  for a variety of chemical species are presented in Table I. Shown in Fig. 2 are  $Z_{\text{eff}}$ 's for perfluorinated alkanes ( $C_nF_{2n+2}$ ) compared with data for alkanes ( $C_nH_{2n+2}$ ) [6]. Also shown are data for CCl<sub>4</sub>, C<sub>2</sub>Cl<sub>6</sub>, and CBr<sub>4</sub>. For fixed molecular polarizability, the annihilation rate is very different for the different compounds.

In searching for an appropriate parameter to describe

these results, we have found that the data come closer to a universal curve when  $\ln(Z_{\text{eff}})$  is plotted as a function of  $(I - I_0)^{-1}$ , where  $I$  is the ionization potential of the molecule in electronvolts [7] and  $I_0$  is 6.8 eV. This is illustrated in Fig. 3(a). The value of 6.8 eV was chosen because this is the binding energy of a positronium (i.e.,  $e^+e^-$ ) atom in its ground state, but we cannot distinguish the value of best fit to better than  $\pm 1$  eV. We have found that  $Z_{\text{eff}}$  for all nonpolar diatomic molecules studied thus far [1-4], with the exception of  $\text{O}_2$ , also fit this empirical scaling [8]. As an example of this, data for the noble gases are included in Fig. 3(a).

We have also studied six-carbon alkene molecules (i.e., compounds similar to alkanes, but with double bonds), to study the effect of different types of chemical bonding on the annihilation rate [9]. As shown in Table I, one double bond increases  $Z_{\text{eff}}$  by a factor of 2, and two double bonds increase  $Z_{\text{eff}}$  by a factor of 4, but a third double bond produces no additional change. We note that these

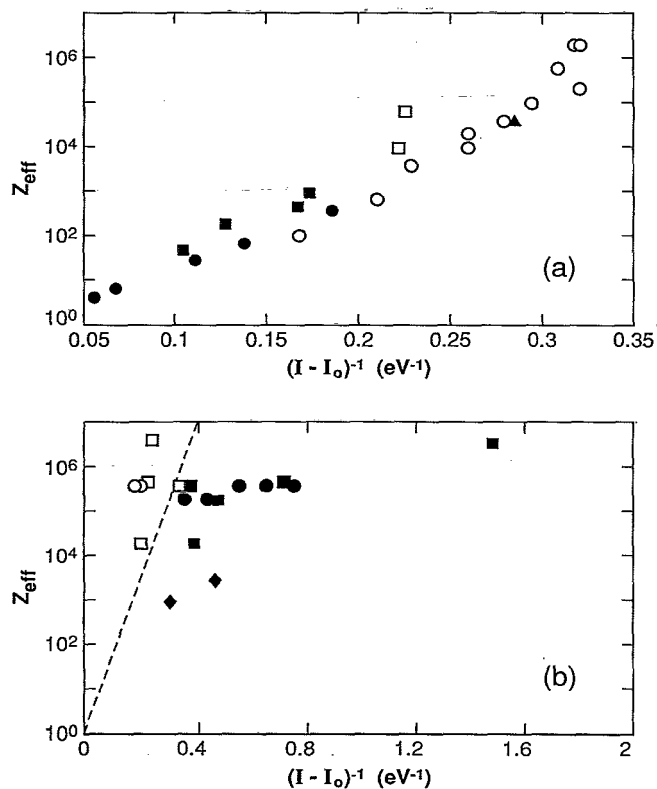


FIG. 3. (a)  $Z_{\text{eff}}$  is shown as a function of  $(I - I_0)^{-1}$ , where  $I$  is the molecular ionization potential and  $I_0$  is 6.8 eV. The symbols are the same as in Fig. 2. Also shown are data for the noble gases ( $\bullet$ ), He through Xe. (b)  $Z_{\text{eff}}$  data are shown as a function of  $(I - I_0)^{-1}$ : hexenes (circles), hydrocarbon rings (squares), and fluorinated rings (diamonds). Solid symbols correspond to using the lowest value of ionization potential, and the open symbols are plotted using the ionization potential of the sigma bond, in the cases for which these data are available. The dashed line in (b) is the best fit to the data in (a).

changes are small, compared with the effect of increasing molecular size.

Comparison of the six-carbon chains with benzene (i.e., a ring,  $\text{C}_6\text{H}_6$ ) indicates another chemical effect: Benzene has a  $Z_{\text{eff}}$  which is a factor of 6 smaller than hexane ( $\text{C}_6\text{H}_{14}$ ), and the double-bonded six-carbon chains have even larger values of  $Z_{\text{eff}}$  than hexane [9]. Adding one methyl group to benzene (i.e., toluene) produces a  $Z_{\text{eff}}$  very similar to hexane. Two- and three-ring compounds have large  $Z_{\text{eff}}$ 's, comparable to alkanes of similar size, so benzene is unique in exhibiting a comparatively low value of  $Z_{\text{eff}}$ . Decahydronaphthalene,  $\text{C}_{10}\text{H}_{18}$ , has a similar  $Z_{\text{eff}}$  to naphthalene,  $\text{C}_{10}\text{H}_8$ , so the localized (as opposed to delocalized) nature of the bonds appears to be a relatively unimportant factor for the case of these two-ring structures, in contrast to the benzene-toluene results.

The scaling of  $Z_{\text{eff}}$  with  $(I - I_0)^{-1}$  fails for the alkanes and the ring compounds when the lowest ionization potential is used [7]. This is illustrated in Fig. 3(b), which shows that  $Z_{\text{eff}}$  is smaller than expected. However, when the ionization potential for the sigma bond is used, the trend is reversed and now  $Z_{\text{eff}}$  is somewhat larger than expected [7].

Perfluorinated ring compounds of benzene, toluene, and naphthalene all have similar  $Z_{\text{eff}}$ 's (800-2600) which are a factor of 20-200 smaller than the analogous hydrocarbons [9]. This is similar to the results for substituted alkanes (i.e., substituted linear chains), where the halocarbons also have lower  $Z_{\text{eff}}$ 's than the hydrocarbons, and they are less sensitive to increases in molecular size.

The data presented here show the importance of molecular structure in determining the interaction of slow positrons with molecules. The scaling of  $Z_{\text{eff}}$  with molecular ionization potential and positronium binding energy suggests that the electronic structure of the positron-molecule complex is important, in contrast to models [3] where molecular vibrations play a dominant role. We are not aware of a theory which adequately describes these results. The extent to which  $I - I_0$  is an important parameter might suggest a model in which a highly correlated positron and electron (resembling a positronium atom) move in the field of a positive ion.

For small, nonpolar molecules, it is thought that there are no positron-molecule bound states [10]. The results presented here suggest that this issue should be reexamined for the case of larger molecules [11].

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(a) Present address: Lawrence Livermore National Laboratory, Livermore, CA 94550.

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- [8] Since  $Z_{\text{eff}}$  is a function of  $\eta^{-1} \equiv (I - I_0)^{-1}$ , it can also be expressed as other functions of  $\eta$ . If the annihilation were due to positronium atom formation by a Maxwellian distribution of hot positrons, we would expect  $\ln(Z_{\text{eff}}) \approx A - B\eta + \frac{1}{2} \ln(\eta)$ . This is not a good fit to the data in Fig. 3(a), and the positron temperature required,  $0.3 \leq B^{-1} \leq 1.0$  eV, is at variance with our measurements [3,5] of  $B$  and with estimates of  $B$  for previous measurements [1,2] of  $Z_{\text{eff}}$ .
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