VOLUME 67, NUMBER 21 PHYSICAL REVIEW LETTERS 18 NOVEMBER 1991

Annihilation of Positrons on Organic Molecules

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(Received 10 September 1991)

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.

PACS numbers: 36.10.−k, 34.50.−s

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 $n=1,2,\ldots$) [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 2×10^{-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

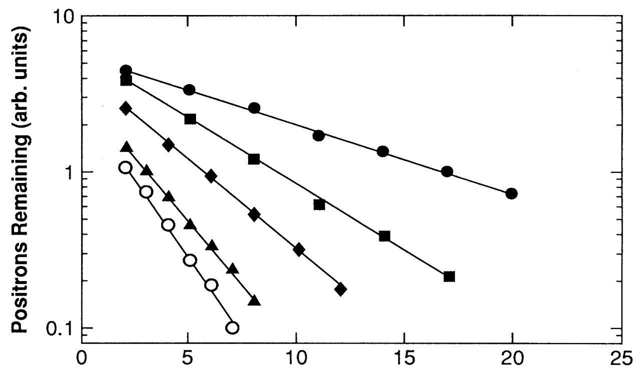

FIG. 1. The number of positrons remaining in the trap as a function of storage time for a 5-s fill when C_8F_{18} is added to the trap at pressures of, ●, 0.00; ■, 0.36; ◆, 0.65; ▲, 1.04; and ○, 1.25 μtorr. The solid lines are least-squares fits to the data.

function of molecular density and is given by $\Gamma = \Gamma_0 + \gamma_1 P_{N_2} + \gamma_x P_x$, where γ_1 and γ_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 Γ_0 is the annihilation rate on other large molecules present as contaminants in the trap. For all of the molecules studied, Γ is found to be linear in P_x as described by the above equation.

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

Molecule	Formula	Z	Z_{eff}
Carbon tetrafluoride	CF_4	42	54.4
Perfluoropropane	C_3F_8	90	151.5
Perfluorohexane	C_6F_{14}	162	535
Octadecafluorooctane	C_8F_{18}	210	1 064
Carbon tetrachloride	CCl_4	74	9 530
Hexachloroethane	C_2Cl_6	114	68 600
Carbon tetrabromide	CBr_4	146	39 800
Hexane	C_6H_{14}	50	98 000
1-hexene	C_6H_{12}	48	185 000
trans 3-hexene	C_6H_{12}	48	196 000
1,3-hexadiene	C_6H_{10}	46	389 000
cis 2, *trans* 4-hexadiene	C_6H_{10}	46	413 000
trans 2, *trans* 4-hexadiene	C_6H_{10}	46	388 000
1,3,5-hexatriene	C_6H_8	44	414 000
Benzene	C_6H_6	42	18 400
Toluene	C_7H_8	50	155 000
Naphthalene	$C_{10}H_8$	68	494 000
Anthracene	$C_{14}H_{10}$	94	4 330 000
Decahydronaphthalene[a]	$C_{10}H_{18}$	78	389 000
Hexafluorobenzene	C_6F_6	90	1 200
Octafluorotoluene	C_7F_8	114	1 240
Octafluoronaphthalene	$C_{10}F_8$	132	3 080

[a]Reference [3].

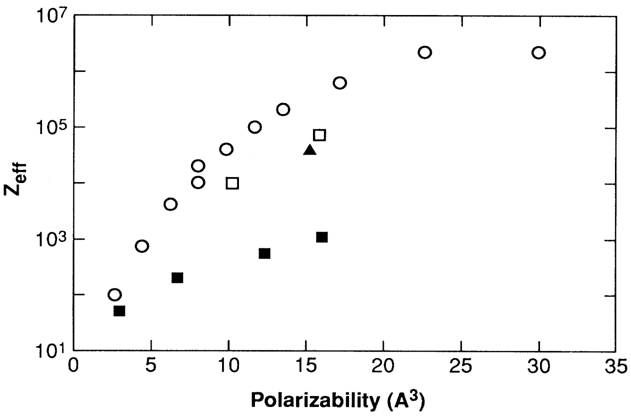

FIG. 2. The annihilation rate per molecule, in units of Z_{eff}, as a function of molecular polarizability for, ○, alkanes (from Refs. [1,3]) and the substituted alkanes, ■, C_nF_{2n+2}; □, C_nCl_{2n+2}; and ▲, C_nBr_{2n+2} (from Table I).

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],

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

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_{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_{eff}, which represents the annihilation rate per molecule. For $Z_{\text{eff}} \gg Z$, one interpretation of the ratio Z_{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_{eff} is conventionally plotted with this as a parameter. However, previous data for Γ_x suggest that there are large differences between different chemical species when molecules with similar molecular polarizabilities are considered [1,3]. For example, SF_6 has a Z_{eff} of 90 as compared with ethane (C_2H_6) with Z_{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_{eff} for a variety of chemical species are presented in Table I. Shown in Fig. 2 are Z_{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_4, C_2Cl_6, and CBr_4. 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 $\ln(Z_{\rm eff})$ 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 ± 1 eV. We have found that $Z_{\rm eff}$ for all nonpolar diatomic molecules studied thus far [1-4], with the exception of 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 $Z_{\rm eff}$ by a factor of 2, and two double bonds increase $Z_{\rm eff}$ by a factor of 4, but a third double bond produces no additional change. We note that these changes are small, compared with the effect of increasing molecular size.

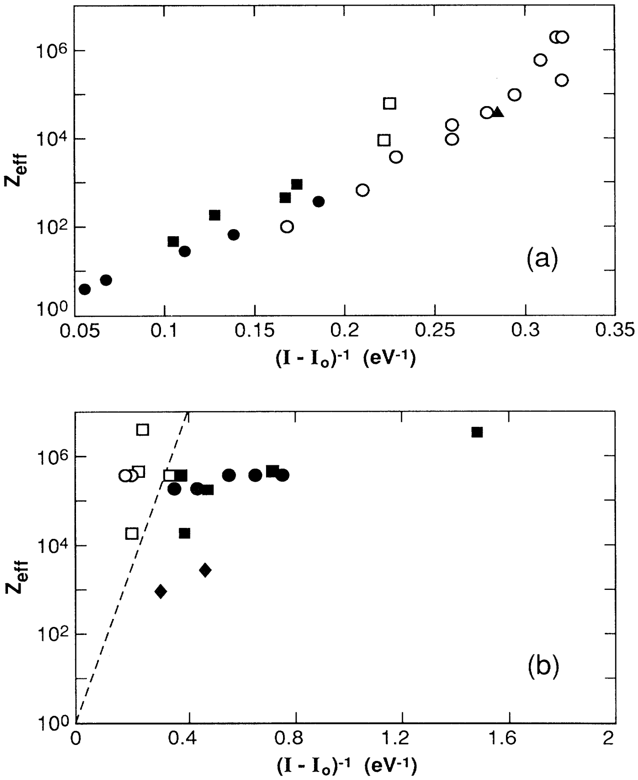

FIG. 3. (a) $Z_{\rm eff}$ is shown as a function of $(I-I_0)^{-1}$, where I is the molecular ionization potential and I_0 is 6.8 eV. The symbols are the same as in Fig. 2. Also shown are data for the noble gases (●), He through Xe. (b) $Z_{\rm eff}$ data are shown as a function of $(I-I_0)^{-1}$: hexenes (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).

Comparison of the six-carbon chains with benzene (i.e., a ring, C_6H_6) indicates another chemical effect: Benzene has a $Z_{\rm eff}$ which is a factor of 6 smaller than hexane (C_6H_{14}), and the double-bonded six-carbon chains have even larger values of $Z_{\rm eff}$ than hexane [9]. Adding one methyl group to benzene (i.e., toluene) produces a $Z_{\rm eff}$ very similar to hexane. Two- and three-ring compounds have large $Z_{\rm eff}$'s, comparable to alkanes of similar size, so benzene is unique in exhibiting a comparatively low value of $Z_{\rm eff}$. Decahydronaphthalene, $C_{10}H_{18}$, has a similar $Z_{\rm eff}$ to naphthalene, $C_{10}H_8$, 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 $Z_{\rm eff}$ 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 $Z_{\rm eff}$ is smaller than expected. However, when the ionization potential for the sigma bond is used, the trend is reversed and now $Z_{\rm eff}$ is somewhat larger than expected [7].

Perfluorinated ring compounds of benzene, toluene, and naphthalene all have similar $Z_{\rm eff}$'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 $Z_{\rm eff}$'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 $Z_{\rm eff}$ 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].

We would like to acknowledge helpful conversations with B. Alder, K. Brueckner, M. Charlton, R. J. Drachman, K. Fagerquist, and J. Onuchic. This work is supported by the Office of Naval Research.

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[8] Since Z_{eff} is a function of $\eta^{-1} \equiv (I - I_0)^{-1}$, it can also be expressed as other functions of η. If the annihilation were due to positronium atom formation by a Maxwellian distribution of hot positrons, we would expect $\ln(Z_{\text{eff}}) \approx A - B\eta + \frac{3}{2}\ln(\eta)$. 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_{eff}.

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[11] Since the measured value of Z_{eff} for xenon (Ref. [5]) is a factor of 2 larger than present calculations and xenon obeys the scaling shown in Fig. 3, reexamination of xenon may also prove useful.