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Measurements of positron-annihilation rates on molecules

K. Iwata, R. G. Greaves, T. J. Murphy,* M. D. Tinkle,† and C. M. Surko
Physics Department, University of California, San Diego, La Jolla, California 92093
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Measurements are presented for the annihilation rates of thermalized positrons in a variety of substances, including noble gases, simple inorganic molecules, hydrocarbons, substituted hydrocarbons, and aromatics. The measurements were performed using trapped clouds of room-temperature positrons, into which substances under test were introduced as low-pressure gases, so that only two-body interactions were involved. These data are compared with other values in the literature, and a compilation of annihilation rates is presented. The measurements illustrate the importance of both chemical composition and the vibrational modes of excitation of the molecules in determining the annihilation rates. The anomalously high annihilation rates observed for large molecules provide evidence for the existence of long-lived resonances. The nature of these resonances is not yet understood, and the data presented are expected to provide useful constraints for the development of theoretical models.

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I. INTRODUCTION

The interaction of positrons with matter is of fundamental importance [1–3]. These interactions have been studied ever since positrons first became available for laboratory experiments [4]. Some aspects of positron-matter interactions are similar to electron-matter interactions, since the positron and the electron have the same mass. Thus, theories developed for electron-matter interactions have been successfully applied to describe many positron-matter interactions. However, positrons can also provide information that is not obtainable from electrons, through such processes as annihilation and positronium atom formation [4]. In this paper, we report a systematic study of positron-molecule interactions at positron energies below the threshold for positronium atom formation. Recent advances in positron trapping techniques [5] have allowed us to extend these measurements to a wide variety of molecular species.

This paper is organized in the following way. In Sec. II, we discuss the nature of the interaction of slow positrons with molecules in two-body collisions, and we describe previous experimental work on the subject. Section III describes the setup of our experiment for measuring annihilation rates using trapped positrons. In Sec. IV, we present annihilation rate data for various molecules, including a comprehensive compilation of earlier results. In Sec. V, we discuss the trends we observe in various chemical families, and we descibe possible factors contributing to these trends. In Sec. VI, we briefly summarize the state of research in this area.

II. POSITRON-MATTER INTERACTIONS

A. Theoretical considerations

Dirac predicted that a positron and an electron with opposite spins could annihilate to produce two quanta of γ radiation [6]. In the nonrelativistic limit, the rate for this process for a positron in a gas of electrons with density n_s of spins opposite to that of the positron is

$$\Gamma_s = 4\pi r_0^2 c n_s, \qquad (1)$$

where r_0 is the classical radius of the electron and c is the speed of light. For an uncorrelated electron gas of density n_e, $n_s = n_e/4$, so that the spin-averaged rate of annihilation for free electrons is

$$\Gamma_e = \pi r_0^2 c n_e. \qquad (2)$$

This formula is frequently modified to describe the annihilation rate Γ in molecular gases by introducing a parameter Z_{eff} into Eq. (2) to represent the effective number of electrons per molecule implied by the observed annihilation rate [7]. Thus,

$$\Gamma = \pi r_0^2 c n Z_{\text{eff}}, \qquad (3)$$

where n is the number density of molecules. The introduction of the parameter Z_{eff} is an attempt to take into account the structure of the atomic or molecular electron wave function and positron-electron correlations.

The annihilation of positrons on small atoms can be understood in terms of simple collisions [8,9]. Empirically, it is found that Z_{eff} for these molecules is of the order of, but somewhat larger than Z, which is the number of electrons in the molecule. In contrast, the annihilation rates for larger organic molecules are observed to be much higher than expected on the basis of such models [8,10–12]. It is believed that this is due to the attachment of positrons to the molecule via long-lived positron-molecule resonances, but the detailed mechanisms of at-

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*Present address: Lawrence Livermore National Laboratory, Livermore, CA 94551.

†Present address: Plasma Physics Laboratory, Columbia University, New York, NY 10027.

tachment and subsequent positron annihilation are not understood [8,10–12]. Previous measurements [8,11–13] give various values of $Z_{\rm eff}/Z$ ranging from order unity to $\sim 10^4$, with anomalously high values for large organic molecules. Experimental values of $Z_{\rm eff}/Z$ for molecules are plotted against Z in Fig. 1, showing the strong dependences of $Z_{\rm eff}/Z$ on the size and chemical composition of the molecules.

The physical process resulting in the observed values of $Z_{\rm eff}$ might be understood qualitatively in the following way. The long-range interaction between the positron and the molecule is attractive, due to the dipole resulting from the positron polarizing the electron cloud in the molecule. At low incident positron energy, this interaction will increase the collision cross section σ_c above the value determined by the size of the molecule. The collision rate Γ_c can be expressed as $\Gamma_c = n\sigma_c v$, where v is the velocity of the positron, and the molecule is assumed to be stationary. When the positron-molecule interaction is a simple elastic collision, the time τ_c spent by the positron in the molecular electron cloud is approximately $\tau_c \sim d/v$, where d is the molecular diameter. The probability of the positron annihilating during the collision may be expected to have the heuristic form $1 - e^{-\tau_c/\tau_0}$, where $1/\tau_0$ is the annihilation rate during the collision. A rough estimate for τ_0 is $\tau_0 \sim 5 \times 10^{-10}$ s, which is the spin-averaged lifetime of a positronium atom [14]. With this assumption, the annihilation rate for such an elastic collision $\Gamma^{\rm el}$ can be expressed as

$$\Gamma^{\rm el} = n\sigma_c v(1 - e^{-\tau_c/\tau_0}). \tag{4}$$

Because $\tau_c \ll \tau_0$, this expression can be approximated as

$$\Gamma^{\rm el} = n\sigma_c v \frac{\tau_c}{\tau_0}. \tag{5}$$

If, on the other hand, we assume that the positron forms a resonance with the molecule, the positron spends the resonance time $\tau_{\rm res}$ in the vicinity of the molecule. Electron-molecule resonances are known to occur with measured values of $\tau_{\rm res}$ as large as 10^{-5} s [15], so we do not assume $\tau_{\rm res} \ll \tau_0$. By analogy with Eq. (4), the annihilation rate for resonance collisions $\Gamma^{\rm res}$ can be expressed as

$$\Gamma^{\rm res} = n\sigma_{\rm res} v(1 - e^{-\tau_{\rm res}/\tau_0}), \tag{6}$$

where $\sigma_{\rm res}$ is the resonance formation cross section. Comparing Eq. (5) and Eq. (6) with the definition of $Z_{\rm eff}$, Eq. (3), we find

$$Z_{\rm eff}^{\rm el} = \frac{\sigma_c v}{\pi r_0^2 c} \frac{\tau_c}{\tau_0}, \tag{7}$$

for annihilation by elastic collisions, and

$$Z_{\rm eff}^{\rm res} = \frac{\sigma_{\rm res} v}{\pi r_0^2 c}(1 - e^{-\tau_{\rm res}/\tau_0}), \tag{8}$$

for annihilation by resonance collisions. For positrons at 300 K, if we assume σ_c is of the order of 10^{-15} cm^2 and consider a simple elastic collision, where τ_c is of the order of 10^{-14} s, then $Z_{\rm eff}^{\rm el} \sim 10$ from Eq. (7). When the collision involves an attachment via long-lived positron-molecule resonances, Eq. (8) can be expressed as

$$Z_{\rm eff}^{\rm res} \sim 10^6 \left(\frac{\sigma_{\rm res}}{10^{-15}\ {\rm cm}^2}\right)(1 - e^{-\tau_{\rm res}/\tau_0}). \tag{9}$$

Thus, $Z_{\rm eff}^{\rm res}$ has its maximum value when $\tau_{\rm res} \geq \tau_0$. If we assume $\sigma_{\rm res}$ of the order of 10^{-15} cm^2, then $Z_{\rm eff}^{\rm res} \sim 10^6$ from Eq. (9). This range of $Z_{\rm eff}$, from 10 to 10^6, is what we have observed. For $Z_{\rm eff} \gg Z$, the quantity $Z_{\rm eff}$ can no longer be interpreted as an effective number of electrons participating in the annihilation process. In this case, $Z_{\rm eff}$ should then be regarded as a normalized annihilation rate.

For the case of electron-molecule resonance collisions, values of $\tau_{\rm res}$ have been calculated successfully [16,17] by applying the Marcus-Rice equilibrium modification (RRKM) of the Rice-Ramsperger-Kassel theory [18], which was developed to describe unimolecular reactions [19]. The RRKM theory is a statistical theory that assumes a rapid statistical redistribution of energy among the various degrees of freedom of the molecule. It is accepted to be the most accurate and practical approximate model for such reactions [18]. The theory has been successfully applied to describe resonance collisions of electrons with selected molecules [16,17], and it may provide quantitative insights into positron-molecule resonance lifetimes and annihilation rates.

With the exception of the estimates given in Refs. [11] and [13], the RRKM theory has not been applied to positron-molecule resonance collisions. For the case of the positron-molecule resonances described here, we envision that the incoming positron transfers its kinetic energy to the vibrational modes of the molecule. If the positron-molecule potential is attractive (i.e., the positron affinity, $\epsilon_A > 0$), then the positron will be bound to the molecule until the vibrational energy is transferred back to the positron. The RRKM theory is able to pre-

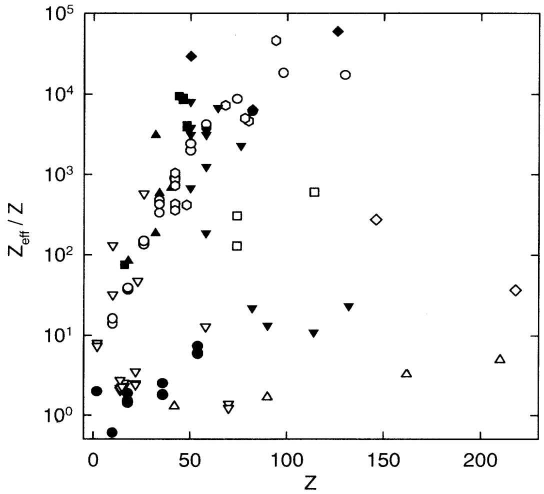

FIG. 1. Experimental values of $Z_{\rm eff}/Z$ plotted against Z: (●) noble gases, (▽) simple molecules, (○) alkanes, (△) perfluorinated alkanes, (□) perchlorinated alkanes, (◇) perbrominated and periodated alkanes, (■) alkenes, (▲) oxygen-containing hydrocarbons, (○) ring hydrocarbons, (▼) substituted benzenes, and (◆) large organic molecules.

dict τ_{res} if the vibrational mode frequencies and ϵ_A are known. For most common molecules, these vibrational frequencies are known. However, at present, very little is known about the positron-molecule affinity, ϵ_A.

B. Earlier measurements

The first measurements of Z_{eff} were made in dense gases. Because pressurized gases were used for these experiments, the variety of molecules tested was limited to those existing as gases at atmospheric or higher pressure. The results of these experiments are reviewed [8,20], and the experimental operation is described in detail elsewhere [21,22]. The technique uses a ^{22}Na radioactive source, which emits a 1.28-MeV γ ray with a negligible delay after the emission of a positron. The positron annihilates in a pressurized gas chamber, and delayed coincidences are observed between signals recorded on scintillation counters from the 1.28-MeV γ ray and the annihilation γ rays. The delay is a measurement of the annihilation rate and is typically of the order of 10^{-8} s in gases at atmospheric pressure.

Positrons emitted from the source typically have energies of a few hundred keV. They rapidly lose energy through ionization and electronic excitation of gas molecules until their energy falls below the threshold energy for electronic excitation. The ionization cross section σ_i at 100 eV is about 10^{-16} cm^2, while the annihilation cross section is

$$\sigma = \frac{\Gamma}{nv} = \frac{\pi r_0^2 c Z_{\text{eff}}}{v}, \qquad (10)$$

and $\sigma \sim 10^{-23} Z_{\text{eff}}$ cm^2 at 100 eV. For these energies, $\sigma \ll \sigma_i$. Therefore, the positrons slow down without significant loss from annihilation at these energy ranges. Further moderation of positrons occurs through elastic collisions in the case of noble gases, and mainly through inelastic vibrational and rotational excitation collisions in the case of polyatomic molecules. In elastic collisions, a positron loses at most a fraction $2m/M$ of its initial energy per collision, where m and M are the masses of the positron and the gas atom, respectively. As a result, about $M/2m$ large-angle elastic collisions are required for thermalization, leading to the definition of an effective thermalization cross section for elastic collisions,

$$\sigma_t^{\text{el}} = \frac{2m\sigma_m}{M}, \qquad (11)$$

where σ_m is the elastic momentum-transfer cross section, which is on the order of atomic dimensions. For polyatomic molecules, vibrational and rotational excitations provide a more efficient thermalization mechanism, and the cross sections σ_t^{inel} are typically around 10^{-16} cm^2 [23]. In order to study the interaction of thermalized positrons with molecules, we must have

$$\frac{\sigma_t}{\sigma} \gg 1. \qquad (12)$$

For noble gases,

$$\frac{\sigma_t^{\text{el}}}{\sigma} \sim \frac{10^3}{M Z_{\text{eff}}}, \qquad (13)$$

where M is in atomic mass units, while for polyatomic molecules,

$$\frac{\sigma_t^{\text{inel}}}{\sigma} \sim \frac{10^5}{Z_{\text{eff}}}. \qquad (14)$$

Thus, thermalization occurs before annihilation for small noble gases, such as helium and neon, and for polyatomic molecules with $Z_{\text{eff}} \ll 10^5$. However, these estimates indicate that positrons can annihilate before they reach thermal equilibrium for large noble gases and for some large organic molecules. In particular, Z_{eff} can be as large as 10^2 for large noble gases [8,24–27] and 10^6 for large organic molecules [8,11–13]. Although a mixed-gas technique has been developed to address this thermalization problem [25], it is desirable that positron annihilation on molecules be reexamined experimentally using low-energy positrons.

III. EXPERIMENTAL SETUP

In recent years, positron trapping techniques have been developed [5] in which positrons are trapped in an electrostatic potential well by inelastic collisions with small molecules such as N_2. This method circumvents the thermalization problems encountered in the delayed-coincidence annihilation spectrum measurements in dense gases. In the positron trap, the thermalization of positrons is performed by a tungsten film or solid neon moderator and by inelastic collisions in a nitrogen buffer gas, rather than by the test gas. The thermalized positrons are confined in a region of low buffer gas pressure created by differential pumping. Because the trap is housed in an ultrahigh vacuum system, molecules that exist as liquids or solids at atmospheric pressure can be introduced into the system as low-pressure vapors for annihilation studies, thus extending the variety of chemical species to be tested as compared to dense-gas experiments.

The measurements presented here were performed in a positron trap [28], using techniques similar to those described in our earlier studies [11–13,27–29]. Details of the operation of the trap and of the trapping mechanism are presented elsewhere [5]. Radial confinement of positrons in the trap is achieved using a magnetic field. Axial confinement is provided by an electrostatic potential well imposed by the voltages on a set of cylindrical and hyperboloidal confining electrodes. The trap accumulates positrons from a low-energy positron beam, storing room-temperature positrons for times of the order of 1 min in the presence of the buffer gas and for more than one half an hour if the buffer gas feed is switched off after the positrons are trapped [30].

The principle of the positron trap is illustrated in Fig. 2. The trap was developed specifically to achieve high efficiency in accumulating and storing a large number of thermalized positrons. Positrons from a 70-mCi ^{22}Na source are moderated using a 1-μm-thick, single-crystal tungsten transmission moderator [31,32] or a solid neon moderator [33] biased to form a 40-eV positron beam. The positrons are then guided magnetically into the trap-

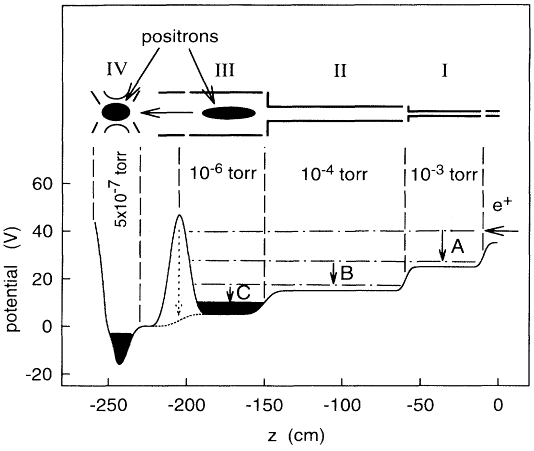

FIG. 2. Schematic diagram of the four-stage positron trap, showing the electrode structure and the inelastic collisions (A, B, and C) in the potential well which lead to positron trapping. The positrons accumulated in stage III are shuttled to stage IV by lowering the potential barrier between these two stages, as indicated by the dotted lines.

ping region, where they are trapped by inelastic collisions with a nitrogen buffer gas. The pressure of the nitrogen gas in stage I is adjusted so that, on average, the positrons experience one inelastic electronic excitation or ionization collision (labeled A in Fig. 2) upon traversing the length of stage I. The energy lost in such a collision is large enough that they become trapped within the electrode structure. Subsequent electronic excitation collisions (B and C in Fig. 2) result in the positrons becoming confined to stages II and III in less than 1 ms, and finally in stage III in a time of the order of 30 ms [5]. The positrons are then shuttled to stage IV by dropping the potential barrier between stages III and IV, as shown in Fig. 2. They cool to room temperature, the temperature of the nitrogen gas, in a characteristic time of about 1 s, through vibrational and rotational excitations of nitrogen molecules. Currently, we are able to accumulate on the order of 10^8 positrons with a 70-mCi ^{22}Na source using a solid neon moderator [34].

Use of the positron trap for annihilation studies has important advantages over the delayed-coincidence annihilation spectrum measurements in dense gases. As described above, earlier measurements of annihilation rates, which use the test gas for the thermalization of fast positrons [8,10,22,24–26,35–38], suffer uncertainty in the positron energies at the moment of the annihilation [25,27]. It has been shown experimentally and theoretically that Z_{eff} is a function of positron energy and decreases as energy increases [25,39]. The thermalization time is found to depend on the molecules used. As expected, it is especially long for noble gases, for which only elastic collisions are available. In contrast, thermalization of positrons in our positron trap is accomplished by the nitrogen buffer gas, and the process is well characterized [5]. Differential pumping of the system enables us to create a region of low nitrogen pressure where positrons can be stored and where annihilation with the test gas occurs with a characteristic annihilation time longer than the thermalization time. We can independently measure and control the positron temperature [30,40] so that there is no ambiguity in positron energy. Measurements of the dependence of annihilation rates on positron temperature are also possible, but have not yet been carried out.

Various gases and vapors may be introduced directly into stage IV in order to study the annihilation of positrons on these substances. Molecules that exist as liquids or solids at room temperature are introduced in vapor form into the trap. The use of low-pressure gases helps to insure that one is studying a binary process involving one positron and one molecule. This avoids the potential complications due to the clustering of atoms or molecules at the site of the positron before annihilation takes place [41,42]. A diagram of stages III and IV is shown in Fig. 3, including the vacuum and detection systems. Annihilation rates are determined by accumulating positrons for a fixed amount of time in stage III ("filling"), waiting 1 s for positrons to thermalize after they are shuttled to stage IV, and then waiting a variable amount of time while the positrons annihilate with the test gas ("storing"). After this storage time, the remaining positrons are dumped onto a metal annihilation plate, shown in Fig. 3, and the characteristic 511-keV annihilation radiation is measured using a NaI(Tl) scintillator. The light pulse amplitude is proportional to the number of positrons detected. A typical set of data is shown in Fig. 4(a), and the annihilation rate as a function of test gas pressure is shown in Fig. 4(b).

The linear dependence indicated by Fig. 4(b) confirms that the process being studied is a binary encounter between the positron and an atom or molecule of the test gas. In particular, for a binary process, the annihilation rate is given by

$$\Gamma = \Gamma_0 + AP_{\text{N}_2} + BP_X, \qquad (15)$$

where A and B are constants proportional to the Z_{eff} of nitrogen and of the molecule under study, respectively, P_{N_2} and P_X are the pressures at room temperature of these gases, and Γ_0 is the annihilation rate on other large

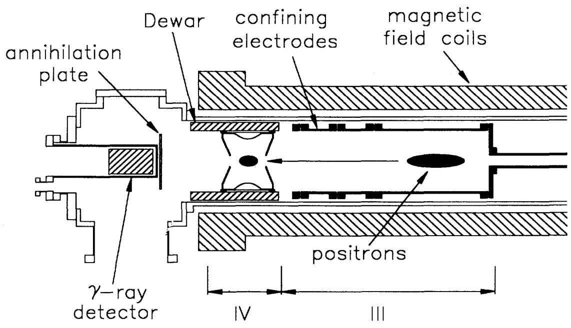

FIG. 3. Schematic diagram showing the final two stages of the positron trap and other equipment used in the annihilation studies.

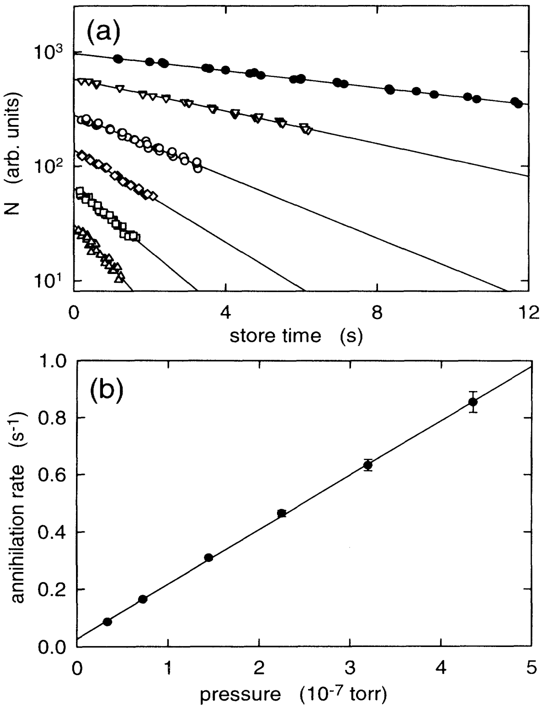

FIG. 4. Data for the annihilation of positrons on benzene-*d*. (a) Number of positrons remaining N as a function of time for various test gas pressures: (•) 3.4×10^{-8}, (▽) 7.3×10^{-8}, (○) 1.5×10^{-7}, (◇) 2.3×10^{-7}, (□) 3.2×10^{-7}, and (△) 4.4×10^{-7} torr. (b) Annihilation rate as a function of test gas pressure, deduced from the data in (a).

molecules present as contamination in the vacuum system. A water-ethanol mixture chilled to −7.5 °C in a Dewar inside the vacuum chamber (shown in Fig. 3) is used to reduce impurities. In the absence of a test gas, the lifetime of positrons is predominantly limited by annihilation with N_2. P_X is measured by a Bayard-Alpert ion gauge. When available, pressure gauge sensitivities in the literature were used [43]. For those that were not available, we measured the sensitivities using a similar technique to that described in Ref. [43]. As a consistency test, we repeated measurements for some of the molecules from Ref. [43], and our results agree to better than 20%.

The molecules used in the measurements reported here were obtained from the Aldrich Chemical Company and were the highest purity commercially available. The liquids were degassed prior to use by repeated freezing and thawing under vacuum. During the experiments, the test liquids were kept at constant temperature, using a water bath to insure stable vapor pressure during the measurements.

IV. RESULTS

In this section, we compare our values of Z_{eff}, measured in low-pressure gases using the positron trapping techniques described above, with those of other groups, who obtained their data in dense gases. The experiments in dense gases [8,10,22,24–26,35–38] were performed at pressures $\geq 10^2$ torr, while our low-pressure experiments [11–13,27–29] were performed at pressures $\leq 10^{-5}$ torr. In general, the values of Z_{eff} in dense gases and those in low-pressure gas experiments agree to within 30%. We also tabulate values of Z_{eff}/Z, which scale Z_{eff} by the number of electrons in the atom or molecule, and they are summarized in Fig. 1. When plotted in this manner, the data show a large scatter. Plotting Z_{eff} as a function of molecular polarizability does not appreciably reduce this scatter, except for small molecules, where a dependence on molecular polarizability was previously noted [12]. In Sec. V, we describe another way of plotting the data which appears to provide more insight into the physical mechanism underlying the annihilation process.

A. Noble gases

Experimentally measured and theoretically calculated values of Z_{eff} for noble gases are listed in Table I and illustrated in Fig. 5. The theoretical calculations based on a polarized orbital model [9] and on a more exact variational model [44] for helium, are in good agreement with the measurements. The polarized-orbital calculation for neon [45] also agrees reasonably well with the measurement. Our values for argon, krypton, and xenon are higher than those reported by other groups for measurements in dense gases. The ratios of the thermalization to the annihilation cross sections calculated from Eq. (13) for argon, krypton, and xenon are 0.8, 0.1, and 0.02, respectively. These values suggest that positrons are not thermalized before annihilation for dense-gas ex-

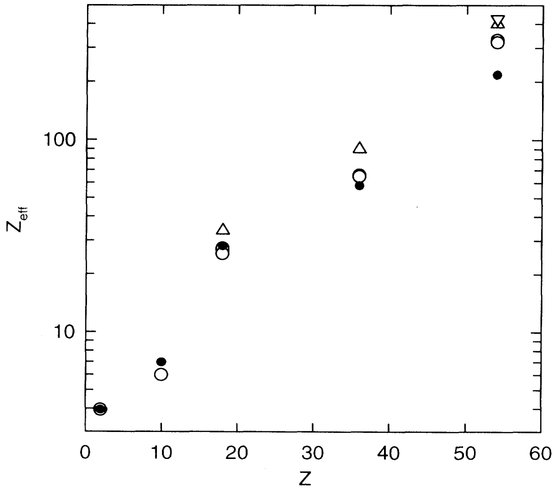

FIG. 5. Theoretical and experimental values of Z_{eff} for noble gases: (•) theoretical values, (△) experimental values measured in the positron trap, (○) values measured in experiments in dense-gases, and (▽) dense gas experiment with H_2 test-gas mixture. The values measured in the positron trap are generally higher than those in dense-gas experiments.

TABLE I. Values of Z_{eff} for noble gases. References are given for previous measurements.

Molecule	Formula	Z	Z_{eff} (Theory)	Z_{eff}	Z_{eff}/Z	Ref.
Helium	He	2	4.02[a],3.84[b]	3.94	2.0	[24]
Neon	Ne	10	6.97[c]	5.99	0.6	[24]
Argon	Ar	18	28[d]	33.8†	1.9	this study
				26.77	1.5	[24]
				27.3	1.5	[35]
				27.1	1.5	[36]
				25.5	1.4	[10]
Krypton	Kr	36	58[e]	90.1†	2.5	this study
				65.7	1.8	[25]
				64.6	1.8	[24]
Xenon	Xe	54	217[e]	401†	7.4	[27]
				330	6.1	[26]
				320	5.9	[25]
				400–450‡	7.4-8.3	[25]
				320	5.9	[8]
				320	5.9	[24]

†Measured in the positron trap, ‡measured in a dense Xe-H_2 gas mixture.

[a] Reference [9].

[b] Reference [44].

[c] Reference [45].

[d] Reference [46].

[e] Reference [47].

periments. A higher-temperature population of positrons would lead to a lower Z_{eff}, according to theoretical calculations [46,47], and the trend of higher values of Z_{eff} measured in our positron trap is consistent with this.

In order to overcome the problem of slow thermalization of positrons in the larger noble gases, Wright *et al.* [25] developed a technique for measuring positron annihilation in dense-gas mixtures. In their experiments, a small admixture of H_2 is used to increase the thermalization rate of the positrons. The Xe-H_2 experiments gave Z_{eff} of 400–450 [25], which agrees with the value obtained in the positron trap [27]. For Kr and Ar, the gas-mixture experiments produced similar results to the pure-gas experiments in dense gases. Our results for Kr and Ar are not in very good agreement with the dense-gas results. We have no definitive explanation of this discrepancy. In principle, systematic errors in our measurements could account for the difference, and more careful measurements for Kr and Ar in the positron trap are planned. We note that the values measured in the positron trap for argon, krypton, and xenon are higher than the theoretical ones (Table I).

B. Inorganic molecules

Values of Z_{eff} for simple inorganic molecules are listed in Table II. Polar and nonpolar molecules are tabulated separately. At separations much larger than molecular dimensions, the long-range interaction between a positron and a polar molecule is a dipole interaction with force proportional to p/r^3, where p is the permanent molecular dipole moment and r is the separation between the molecule and the positron. This interaction is stronger than that between a positron and a nonpolar molecule, for which the positron polarizes the molecular electron cloud, inducing a dipole moment and producing a force proportional to α/r^4, where α is the polarizability of the molecule. Because of the strong, long-range nature of the interaction for polar molecules, we expect these species to have higher values of Z_{eff} than those of similar nonpolar molecules. The molecular dipole moments [48] are also listed in Table II, and it can be seen that polyatomic polar molecules have relatively large values of Z_{eff}, with $Z_{\text{eff}}/Z > 10$, with the exception of nitrous oxide which has a small dipole moment. For nonpolar substances, a correlation between Z_{eff} and polarizability for some chemical species has been reported earlier [12,49].

Because of the structural complexity of polyatomic molecules, theoretical values of Z_{eff} are available only for a limited number of these substances [50]. Positron annihilation on H_2 has been extensively studied because of the relative simplicity of its structure. A calculation using the Kohn variational method yields a Z_{eff} of 10.7 [51], which is smaller than the experimental values (see Table II). The calculation for N_2 using polarization potentials with a phenomenological cutoff gives $Z_{\text{eff}} = 18$ [52]. This value is smaller than the experimental values. *Ab initio* calculations using the Kohn variational method for N_2 are currently being investigated [53]. The calculation for NH_3 with the fixed-nuclei approximation and without the polarization of molecular orbitals due to the incoming positrons gives $Z_{\text{eff}} = 241$, while the calculation including the polarization increases the value to about 500 [54], which is still much smaller than the experimental value of 1300 [8].

TABLE II. Measured values of Z_{eff} for inorganic molecules. The values of dipole moment DM have units of debye (D).

Molecule	Formula	Z	Z_{eff}	Z_{eff}/Z	DM (D)^{a}	Ref.
Diatomic molecules (nonpolar)						
Hydrogen	H_2	2	14.6	7.3		[38]
			16.02	8.0		[25]
			14.7	7.4		[8]
Deuterium	D_2	2	14.7	7.4		[8]
Nitrogen	N_2	14	30.5	2.2		[8]
			28.9	2.1		[37]
Oxygen	O_2	16	36.7†	2.3		this study
			40.5	2.5		[8]
Diatomic molecules (polar)						
Carbon monoxide	CO	14	38.5	2.8	1.96	[8]
Nitric oxide	NO	15	34	2.3	1.7	[8]
Polyatomic molecules (nonpolar)						
Carbon dioxide	CO_2	22	54.7	2.5		[25]
			53	2.4		[8]
Sulfur hexafluoride	SF_6	70	86.2†	1.2		this study
			97	1.4		[8]
Polyatomic molecules (polar)						
Ammonia	NH_3	10	1 300	130	1.47	[8]
Water	H_2O	10	319†	32	1.85	this study
Nitrous oxide	N_2O	22	78	3.5	0.167	[8]
Nitrogen dioxide	NO_2	23	1 090	47	0.316	[8]
Methyl chloride	CH_3Cl	26	15 000	580	1.87	[8]
Dichlorodifluoromethane	CCl_2F_2	58	750	13	0.51	[22]

†Measured in the positron trap.

^{a}Reference [48].

C. Alkanes and substituted alkanes

Values of Z_{eff} for alkanes and substituted alkanes are listed in Table III and values of Z_{eff}/Z are plotted against Z in Fig. 1. For alkanes, Z_{eff}/Z increases from ~ 10 for methane to $\sim 2\times10^4$ for hexadecane. These anomalously high values of Z_{eff}/Z might be explained by long-lived resonances [11]. We note that Z_{eff}/Z does not increase between dodecane and hexadecane.

Theoretical calculations of Z_{eff} for CH_4 are available [54]. Using the fixed-nuclei approximation, the values are 46.8 without including the polarization of the molecular orbitals, and 99.5 with the polarization. These values are smaller than the experimental values (see Table III).

Substitution of hydrogen atoms in the alkanes by other atoms dramatically changes Z_{eff}. Substitution by fluorine decreases Z_{eff}, while substitution by iodine, chlorine, or bromine increases Z_{eff} by differing amounts.

D. Alkenes

Table IV gives values of Z_{eff} for various alkenes. The molecular structures and values of Z_{eff} are illustrated in Fig. 6. Introducing one double bond into the alkanes ethane and hexane, to form ethylene and hexene, respectively, has the effect of approximately doubling Z_{eff}. In the case of hexene, there is no strong dependence of Z_{eff} on the location of the double bond. Introducing a second double bond into hexene to form hexadiene further increases Z_{eff} by approximately another factor of 2. Once again, there is no significant isomeric dependence. In-

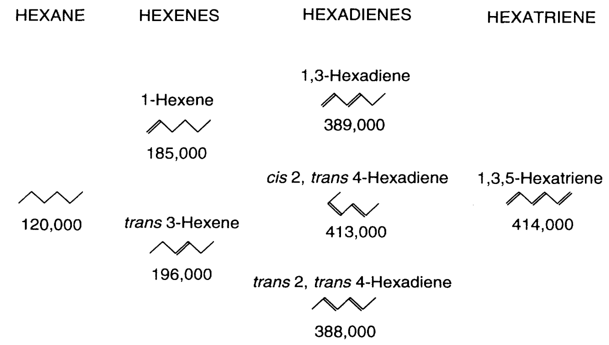

FIG. 6. Values of Z_{eff} and structures of alkenes with six carbons.

troduction of a third double bond does not change Z_{eff} appreciably as compared to hexadiene.

E. Oxygen-containing hydrocarbons

Values of Z_{eff} for alcohols, carboxylic acids, and ketones, which have not been studied previously, are listed in Table V. The measurements were an effort to observe chemical trends of Z_{eff} in molecules containing oxygen. Alcohols, carboxylic acids, and ketones each have values of Z_{eff}/Z approximately an order of magnitude higher than do alkanes with the same number of carbon atoms. For the three-carbon family of these molecules, we find that acetone, which has a C=O group, has the highest Z_{eff}/Z, and that propionic acid, which has both O–H and C=O groups, has slightly higher Z_{eff}/Z than 1-propanol, which has an O–H group. The large dipole moment of acetone (Table V) may be responsible for its high Z_{eff}/Z value.

F. Aromatics and saturated rings

Values of Z_{eff} for ring hydrocarbons, substituted rings, aromatics, and other organic molecules are given in Table VI. Forming hexane into the cyclic ring compound, cyclohexane, dramatically reduces the value of Z_{eff}. A similar decrease is noted when the symmetric ring, benzene, is compared with hexane. The similar values of Z_{eff} for benzene and for cyclohexane, compared with the large value for hexane, suggest that symmetry plays a more important role in determining the value of Z_{eff} than does

TABLE III. Measured values of Z_{eff} for alkanes and substituted alkanes.

Molecule	Formula	Z	Z_{eff}	Z_{eff}/Z	Ref.
Alkanes					
Methane	CH_4	10	142	14	[25]
			140	14	[8]
			162	16	[10]
Ethane	C_2H_6	18	660	37	[8]
			698	39	[10]
Propane	C_3H_8	26	3 500	130	[8]
			3 850	150	[10]
Butane	C_4H_{10}	34	11 300†	330	[13]
			15 000	440	[8]
			16 300	480	[10]
Isobutane	C_4H_{10}	34	14 400	420	[10]
Pentane	C_5H_{12}	42	37 800†	900	[13]
Hexane	C_6H_{14}	50	120 000†	2 400	[29]
			98 200†	2 000	[12]
Heptane	C_7H_{16}	58	242 000†	4 200	[13]
Nonane	C_9H_{20}	74	643 000†	8 700	[13]
Decane	$C_{10}H_{22}$	82	507 000†	6 200	this study
Dodecane	$C_{12}H_{26}$	98	1 780 000†	18 000	[13]
Hexadecane	$C_{16}H_{34}$	130	2 230 000†	17 000	[13]
Deuterated alkanes					
d-Heptane	C_7D_{16}	58	197 000†	3 400	[13]
Perfluorinated alkanes					
Carbon tetrafluoride	CF_4	42	54.4†	1.3	[12]
Perfluoropropane	C_3F_8	90	152†	1.7	[12]
Perfluorohexane	C_6F_{14}	162	535†	3.3	[12]
Perfluorooctane	C_8F_{18}	210	1 064†	5.1	[12]
Perchlorinated alkanes					
Carbon tetrachloride	CCl_4	74	9 530†	130	[12]
			22 500	300	[10]
Hexachloroethane	C_2Cl_6	114	68 600†	600	[12]
Perbrominated alkanes					
Carbon tetrabromide	CBr_4	146	39 800†	270	[12]
Periodated alkanes					
Carbon tetraiodide	CI_4	218	7 990†	37	this study

†Measured in the positron trap.

TABLE IV. Measured values of Z_{eff} for alkenes.

Molecule	Formula	Z	Z_{eff}	Z_{eff}/Z	Ref.
Ethylene	C_2H_4	16	1 200†	75	[29]
1-hexene	C_6H_{12}	48	185 000†	3 900	[12]
trans 3-hexene	C_6H_{12}	48	196 000†	4 100	[12]
1,3-Hexadiene	C_6H_{10}	46	389 000†	8 500	[12]
cis-2, *trans*-4-hexadiene	C_6H_{10}	46	413 000†	9 000	[12]
trans-2, *trans*-4-hexadiene	C_6H_{10}	46	388 000†	8 400	[12]
1,3,5-hexatriene	C_6H_8	44	414 000†	9 400	[12]

†Measured in the positron trap.

the presence of double bonds or delocalized electrons [29]. We note, however, that both benzene and cyclohexane lack methyl groups, which might be the reason that Z_{eff} is lower in these molecules than in hexane. As in the case of the alkanes, perfluorinating aromatic hydrocarbons to form such compounds as octafluoronaphthalene, hexafluorobenzene, and octafluorotoluene results in a dramatic decrease in Z_{eff}.

Deuteration of benzene provides unique information about the annihilation process. Deuteration of molecules does not change their electronic structure, but significantly changes the vibrational modes of the molecules. The structures of the deuterated benzenes studied are illustrated in Fig. 7. As can be seen, deuteration of benzene increases Z_{eff}. Benzene-d_6 (i.e., C_6D_6) has the same number of vibrational modes as does benzene, but they have lower frequencies. Benzene-d_6 shows an increase in Z_{eff} by a factor of 2 over that of benzene, suggesting that positrons interact more strongly with these lower-frequency modes. Benzene-*d* (i.e., C_6H_5D) has the largest number of nondegenerate modes among the deuterated benzenes we have studied, and this molecule has a higher value of Z_{eff} than does either benzene or benzene-d_6. Benzene-1,3,5d_3 has the highest Z_{eff} value, even though it has a smaller number of nondegenerate modes than does benzene-*d*. The high Z_{eff} value for benzene-1,3,5d_3 may arise because it has lower-frequency vibrational modes than does benzene-*d*. Also, it is possible that some modes may not contribute to resonance formation because of selection rules analogous to those observed in electron-benzene resonance collisions [55].

There is one deuteration result that contradicts the trend observed in the deuteration studies for benzene. We had previously measured Z_{eff} for deuterated heptane [13] (see Table III) and found that it was smaller than that of heptane. We plan to repeat this measurement and to carry out additional deuteration experiments to clarify this issue.

We have studied a number of substituted benzene compounds, and Fig. 8 contains a summary of these results. Substituting one hydrogen atom in the benzene molecule with any other functional group increases Z_{eff}. This is true even for –F, which usually has the property of reducing Z_{eff} when substituted for hydrogen atoms. This phenomenon points to the importance of molecular symmetry in reducing Z_{eff} in ring compounds. The magnitude of the increase shows a wide variation, depending on the functional group being substituted, varying from a factor of 2 for –F to a factor of 30 for $-NO_2$. In the latter case, the large dipole moment introduced by the $-NO_2$ substitution may also contribute to the increase in Z_{eff} (Table VI). Substituting one, four, or five additional –F in C_6H_5F decreases Z_{eff} monotonically, which is consistent with the observation that perfluorocarbons have much lower values of Z_{eff} than the analogous hydrocarbons.

TABLE V. Measured values of Z_{eff} for alcohols, carboxylic acids, and ketones.

Molecule	Formula	Z	Z_{eff}	Z_{eff}/Z	DM (D)^a	Ref.
Alcohols						
Methanol	CH_3OH	18	1 510†	84	1.70	this study
1-propanol	$C_2H_5CH_2OH$	34	19 900†	590	1.68	this study
Carboxylic acids						
Acetic acid	CH_3COOH	32	5 880†	180	1.74	this study
Propionic acid	C_2H_5COOH	40	27 200†	680	1.75	this study
Ketones						
Acetone	CH_3COCH_3	32	98 400†	3, 100	2.88	this study

†Measured in the positron trap.

^{a}Reference [48].

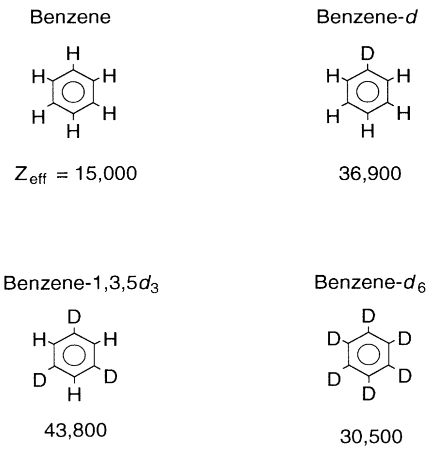

FIG. 7. Values of Z_{eff} and structures of deuterated benzenes studied. Deuterated benzenes have higher values of Z_{eff} as compared to the ordinary benzene, indicating the importance of the vibrational modes of the molecules in determining Z_{eff}.

In order to test the effect of isomeric symmetry, we measured Z_{eff} of xylene isomers (i.e., benzene rings with two substituted $-CH_3$ groups in various relative positions). The Z_{eff} for *para*-, *ortho*-, and *meta*-xylenes are all identical to within the accuracy of the measurements, and they are not significantly different from toluene. It appears that once the symmetry of the benzene ring is broken by the addition of a methyl group, further substitutions do not have a strong effect. *Para*-, *ortho*-, and *meta*-xylenes have different but small dipole moments. If the isomeric symmetry is not significant in determining Z_{eff}, as the xylene data suggest, studies of isomeric symmetry using molecules with larger dipole moments, such as dinitrobenzenes, may give us information about the contribution of the molecular dipole moment to Z_{eff} for these molecules, without significantly changing other properties of the molecules.

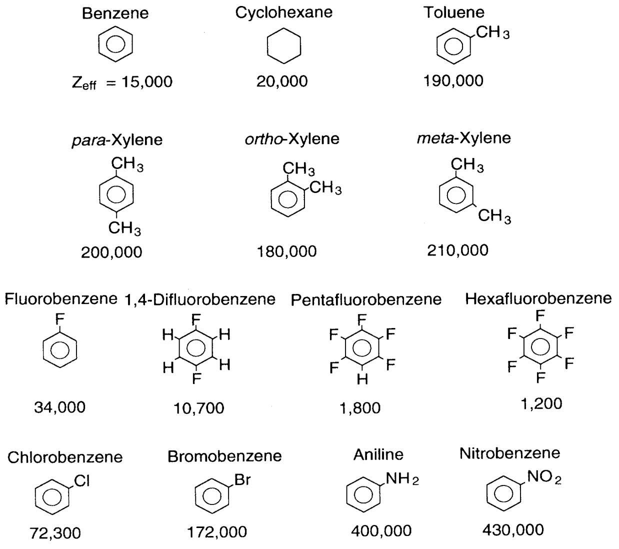

FIG. 8. Values of Z_{eff} and structures of cyclohexane and substituted bezenes. Substitution of one hydrogen atom by any functional group increases Z_{eff}, indicating the importance of molecular symmetry in reducing Z_{eff} in ring compounds.

An important factor in the conventional chemistry of substituted benzenes is whether the substituted group donates or withdraws electrons from the ring. Functional groups such as $-CH_3$, which donate electrons to the ring, tend to activate the ring for electrophilic substitution of a second group, and they induce that substitution to occur at the *ortho* and *para* positions. On the other hand, electron-withdrawing groups like $-NO_2$ tend to deactivate the ring, and to direct substitution to the *meta* position. Our data show no evidence that this effect influences the value of Z_{eff}. For example, the *meta*-director $-NO_2$ produces a value of Z_{eff} similar to that resulting from the *ortho*-, *para*-director $-NH_2$, while –Cl, –Br, –F, $-CH_3$, and $-NH_2$, which are all *ortho*-, *para*-directors, have very different values of Z_{eff}.

We note that the values of Z_{eff}/Z for some large molecules, such as anthracene, glycerol, and sebacic acid dimethyl ester, are higher than those of large alkanes, in which Z_{eff} values are saturated, namely those of dodecane and hexadecane. In the framework of the model described by Eq. (9), this might imply that values of σ_{res} for these molecules are larger than those for large alkanes.

V. DISCUSSION

The relatively simple atomic structure of the noble gases provides a test of our understanding of low-energy positron-atom interactions. Even in this case, there are discrepancies between experimental values measured in the positron trap and theoretical values based on polarized orbital calculations [47] (see Table I) for the case of krypton and xenon. The data presented here indicate that reexamination of the theory might be warranted.

For earlier studies, only a small number of positrons were available, and consequently, uncertainties of a factor of two are possible in the measured values of Z_{eff} [11]. Subsequently, considerably more positrons have become available, and the main source of error is now the 20% uncertainty in the pressure of the test gas. It is likely that the early measurement of Z_{eff} of nonane (see Table III) is higher than the recent measurement of Z_{eff} of decane for this reason.

As a result of earlier studies, it was suggested that the reduction of Z_{eff} in benzene as compared with hexane might be due to the presence of delocalized π-bonding electrons in the benzene ring [12]. However, measurements for cyclohexane, which contains no delocalized electrons, yield a value for Z_{eff} similar to benzene, indicating that delocalized electrons may not be responsible for this effect.

We had previously discovered a linear relationship between $\log_{10}(Z_{\text{eff}})$ and $(E_i - E_{\text{Ps}})^{-1}$ for molecules without double bonds [12], where E_i is the ionization potential of the molecule [56–59], and $E_{\text{Ps}} = 6.8$ eV is the binding energy of a positronium atom. This relationship holds for alkanes, substituted alkanes, noble gases, and all nonpolar molecules studied thus far and is illustrated in Fig. 9. It should be noted that plotting the data as any function of E_i would also collapse the data on a single curve. Choosing $(E_i - E_{\rm Ps})^{-1}$ results in the curve approximating a straight line on a semi-logarithmic plot. We know of no theory that explains this relationship; however, we previously pointed out that this empirical scaling might suggest a model in which a positronium atom moves in the electrostatic field of a positive ion [12].

We reported that the linear relation between $\log_{10}(Z_{\rm eff})$ and $(E_i - E_{\rm Ps})^{-1}$ does not hold for molecules with double bonds [12]. However, some of these molecules do come close to the linear relation, as shown in Fig. 10. This figure shows data for oxygen-containing hydrocarbons and simple molecules with dipole moments and/or double bonds. Oxygen-containing hydrocarbons lie slightly below the line. Most of the simple molecules lie close to the line, with the exception of O_2, NH_3, NO_2, and NO. We are not able to identify any systematic trends for these molecules.

Figure 11 shows the same plot for alkenes, ring hydrocarbons, and substituted benzenes. The majority of these molecules are quite far from the line, and $Z_{\rm eff}$ values seem to reach a saturation around $Z_{\rm eff} \approx 5 \times 10^5$ for alkenes and substituted benzenes. This saturation may be a result of a positron-molecule resonance time $\tau_{\rm res}$ being larger than the spin-averaged annihilation time for a positronium atom (i.e., in the notation of Sec. II A, $\tau_{\rm res} \geq \tau_0$), which, as discussed in Sec. II, might lead to such a saturation. The value of $Z_{\rm eff}$ for anthracene is an order of magnitude larger than this saturated value, which could possibly be explained as follows: $Z_{\rm eff}$ de-

TABLE VI. Measured values of $Z_{\rm eff}$ for ring molecules, aromatics, and other organic molecules.

Molecule	Formula	Z	$Z_{\rm eff}$	$Z_{\rm eff}/Z$	DM (D)[a]	Ref.
Ring hydrocarbons						
Benzene	C_6H_6	42	15 000†	360	0.00	[29]
			18 000†	430	0.00	[12]
Cyclohexane	C_6H_{12}	48	20 000†	420	0.00	[29]
Cyclodecane	$C_{10}H_{20}$	80	369 000†	4 600	0.00	this study
Naphthalene	$C_{10}H_8$	68	494 000†	7 300	0.00	[12]
Decahydronaphthalene	$C_{10}H_{18}$	78	389 000†	5 000	0.00	[13]
Anthracene	$C_{14}H_{10}$	94	4 330 000†	46 000	0.00	[12]
Substituted rings						
Octafluoronaphthalene	$C_{10}F_8$	132	3 080†	23	0.00	[12]
Deuterated benzenes						
Benzene-*d*	C_6H_5D	42	36 900†	880	0.00	this study
Benzene-1,3,5d_3	$C_6H_3D_3$	42	43 800†	1 000	0.00	this study
Benzene-d_6	C_6D_6	42	30 500†	730	0.00	this study
Substituted benzenes						
Toluene	$C_6H_5(CH_3)$	50	190 000†	3 800	0.36	[29]
			155 000†	3 100	0.36	[12]
			189 000†	3 800	0.36	[13]
para-xylene	$C_6H_4(CH_3)_2$	58	200 000†	3 400	0.00	[29]
ortho-xylene	$C_6H_4(CH_3)_2$	58	180 000†	3 100	0.62	[29]
meta-xylene	$C_6H_4(CH_3)_2$	58	210 000†	3 600	N/A	[29]
Aniline	$C_6H_5NH_2$	50	400 000†	8 000	1.53	[29]
Nitrobenzene	$C_6H_5NO_2$	64	430 000†	6 700	4.22	[29]
Chlorobenzene	C_6H_5Cl	58	72 300†	1 200	1.69	this study
Bromobenzene	C_6H_5Br	76	172 000†	2 300	1.70	this study
Fluorobenzene	C_6H_5F	50	34 000†	680	1.60	[29]
1,4-Difluorobenzene	$C_6H_4F_2$	58	10 700†	180	0.00	this study
Pentafluorobenzene	C_6HF_5	82	1 800†	22	N/A	[29]
Hexafluorobenzene	C_6F_6	90	1 200†	13	0.00	[12]
Octafluorotoluene	$C_6F_5(CF_3)$	114	1 240†	11	N/A	[12]
Other organic molecules						
Tetraethylsilane	$Si(C_2H_5)_4$	82	524 000†	6 400	0.00	this study
Glycerol	$C_3H_8O_3$	50	1 470 000†	29 000	N/A	[13]
Sebacic acid dimethyl ester	$C_{12}H_{22}O_4$	126	7 560 000†	60 000	N/A	[13]

†Measured in the positron trap.

[a] Reference [48].

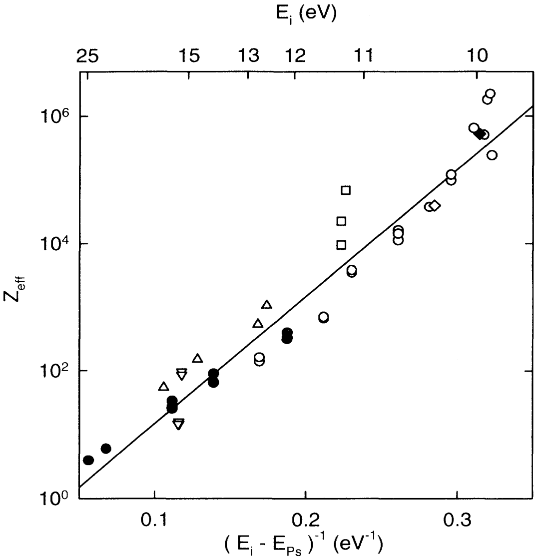

FIG. 9. Values of $Z_{\rm eff}$ for molecules containing only single bonds are plotted against $(E_i - E_{\rm Ps})^{-1}$, where E_i is ionization potential of molecule (labeled on top of graph), and $E_{\rm Ps} = 6.8$ eV is the binding energy of a positronium atom: (●) noble gases, (▽) simple nonpolar molecules, (○) alkanes, (△) perfluorinated alkanes, (□) perchlorinated alkanes, (◇) perbrominated alkane, and (◆) tetraethylsilane. The solid line is a linear regression to the data. The ionization potentials of perchlorinated alkanes and the largest alkanes are not known accurately, which could account for larger deviations from the line for these molecules.

pends both on the resonance formation cross section $\sigma_{\rm res}$ and the resonance time $\tau_{\rm res}$ as shown in Eq. (6). An order of magnitude increase in $\sigma_{\rm res}$ is reasonable for a large molecule such as anthracene as compared with the alkenes, substituted benzenes, and naphthalene, which could account for the higher saturation value of $Z_{\rm eff}$.

Annihilation rate measurements in deuterated benzenes suggest that the vibrational modes are important in determining $Z_{\rm eff}$. At present, it is not understood in detail how the positrons interact with these molecular vibrational modes. The observed changes in $Z_{\rm eff}$ due to changes in the vibrational modes suggest that the application of the RRKM theory (described in Sec. II A) to the positron-molecule resonance collisions may be fruitful. At this point, the major impediment is lack of knowledge of the positron affinity, ϵ_A.

The localization of the positron in a resonance with the molecule is crucial in understanding the trends in $Z_{\rm eff}$ for different chemical species. If the positron stays in a region of high electron density within the molecule during the resonance, a higher value of $Z_{\rm eff}$ is expected. For long-lived resonances, the site of binding will determine ϵ_A. This kind of information can be obtained from studies of the Doppler broadening of the 511-keV annihilation γ-ray line. The earliest study of this type concentrated on hydrogen, because of its importance in the production of astrophysical positron-annihilation radiation [60]. Recently, we began more comprehensive studies of the energy spectra of annihilation radiation in a variety of molecules, including hydrocarbons and perfluorocarbons [61]. These studies suggest that, for the case of hydro-

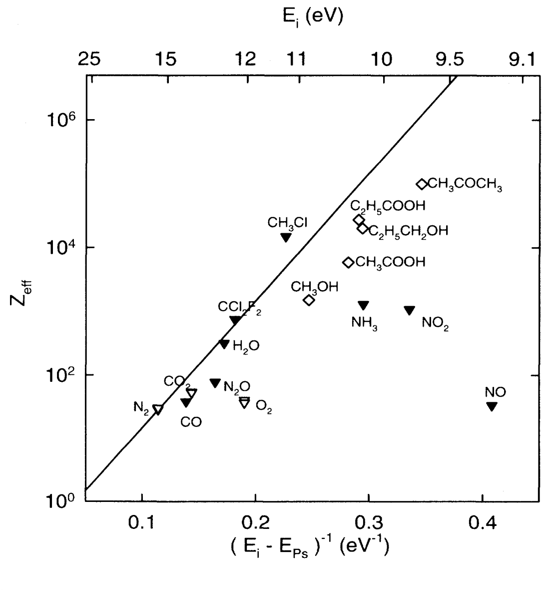

FIG. 10. Values of $Z_{\rm eff}$ plotted against $(E_i - E_{\rm Ps})^{-1}$ for oxygen-containing hydrocarbons and small molecules with a dipole moment and/or double bonds: (▽) simple nonpolar molecules with double bonds, (▼) simple polar molecules, and (◇) oxygen-containing hydrocarbons. The solid line is the linear regression from Fig. 9.

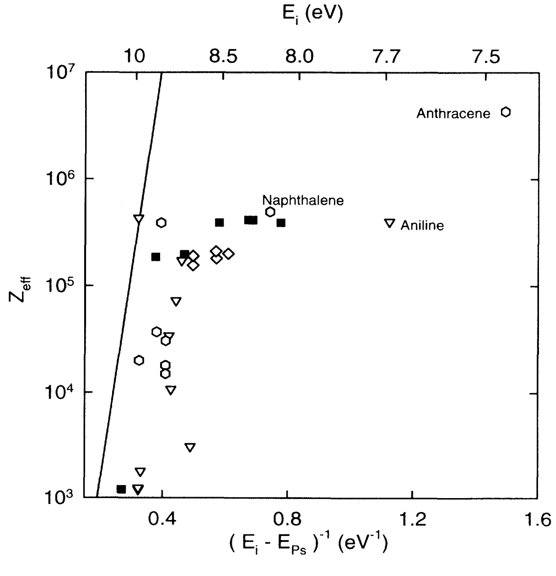

FIG. 11. Values of $Z_{\rm eff}$ plotted against $(E_i - E_{\rm Ps})^{-1}$ for alkenes, ring hydrocarbons, and substituted benzenes: (■) alkenes, (○) ring hydrocarbons, (◇) toluene and xylenes and (▽) other substituted benzenes. The solid line is the linear regression from Fig. 9. The range of $(E_i - E_{\rm Ps})^{-1}$ plotted is much larger than those in Figs. 9 and 10.

carbons, including benzene, the positrons are localized at the C–H bond, while for the perfluorocarbons, they reside on the fluorine atoms. These studies are now being extended to include many of the compounds reported in this paper, and it is expected that these data will help in understanding the processes involved in positron-molecule interactions and the resulting annihilation.

The anomalously high values of Z_{eff} observed for many molecules have important implications for astrophysical processes [62]. There is evidence that large organic molecules, such as polycyclic aromatic hydrocarbons, are present in the interstellar medium (ISM) [63–66]. Infrared spectral measurements from the ISM indicate that polycyclic aromatic hydrocarbons (PAH) such as chrysene and pyrene, shown in Fig. 12, are present in the ISM at concentrations of the order of 10^{-7} times that of atomic hydrogen [66]. These molecules are the smallest of the PAH molecules known to be present in the ISM. Their Z_{eff} values have not been measured because of their low vapor pressures. However, by extrapolating our Z_{eff} data for benzene, naphthalene, and anthracene, which are also shown in Fig. 12, we estimate that the Z_{eff} of these molecules are more than 10^6 times greater than that of atomic hydrogen, which is 8.0 [67]. Thus, these molecules may contribute significantly to the annihilation of slow positrons in the ISM, due to their anomalously high Z_{eff}, and this would then be reflected in the 511-keV annihilation γ-ray line shape from the ISM [61,62]. We plan to investigate annihilation properties of these compounds by installing a "hot cell" in our positron trap.

Another technique that can potentially provide information concerning the localization of the positron on molecules is positron ionization mass spectrometry [68–71]. This technique measures the ion fragments produced when a positron annihilates on a molecule. It is unclear, at present, whether this fragmentation is produced by annihilation of bonding electrons or by electron-hole transfer. A theoretical study of the fragmentation of polyatomic molecules was carried out recently, and it supports the electron-hole transfer picture [72]. Further studies will be needed to clarify this point. We are currently developing the capability to perform *in situ* ion cyclotron resonance mass spectrometry [73], which is expected to have a better mass resolution and greater sensitivity than the time-of-flight techniques used in our earlier work [68].

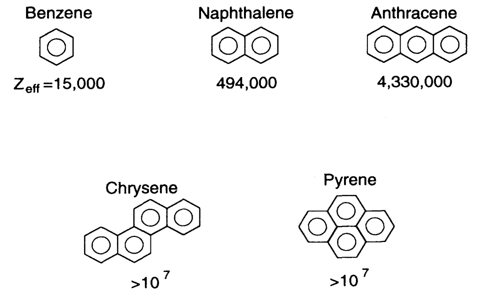

FIG. 12. Molecular structures and Z_{eff} of polycyclic aromatic hydrocarbons. Measured values of Z_{eff} are shown for benzene, naphthalene, and anthracene, and estimated values of Z_{eff} are also indicated for chrysene and pyrene. As discussed in the text, these latter molecules may be significant sources of astrophysical γ-ray radiation from positron annihilation.

VI. CONCLUSIONS

In this paper, we have presented positron-annihilation rates on molecules studied in a positron trap. We have also compared these measurements with those done using other techniques. Where more than one measurement is available for a particular molecule, the data are, in general, in reasonable agreement. The data exhibit a number of chemical trends and illustrate the importance of electronic structure, symmetries, and vibrational modes in the annihilation process. We are not aware of a theory that adequately describes these results.

ACKNOWLEDGMENTS

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