Positron attachment to molecules

J. A. Young[**] and **C. M. Surko[*]

Department of Physics, University of California San Diego, La Jolla, CA 92093, USA

[*] Corresponding author: e-mail csurko@ucsd.edu
[**] e-mail jayoung.physics@gmail.com; present address: Jet Propulsion Laboratory, Pasadena CA, 91109, USA

At incident positron energies below the threshold for positronium atom formation annihilation rates for molecules are much larger than those expected on the basis of simple two-body collisions. We now understand that this phenomenon is due to positron attachment to molecules mediated by vibrational Feshbach resonances. This attachment enhances greatly the overlap of the positron and the molecular electron wave functions and hence increases the probability of annihilation.

Annihilation spectra as a function of incident positron energy yield measurements positron-molecule binding energies. Using this technique, to date, positron-molecule binding energies for thirty molecules have been measured. This paper presents a brief review of our current understanding of this process, the significance of these results, and outstanding questions for future research.

1 Introduction and overview Positron collisions with molecules are important in many contexts. Examples include astrophysics [1], where positrons can interact with molecules in the interstellar medium [2]; medicine, in the context of positron emission tomography (PET); and materials science where positrons are a method of choice to study properties of both metals and insulators [3, 4]. Remarkably, outstanding questions regarding the interaction of positrons with molecules, first raised in the seminal experiments of Deutsch in 1951 [5] and more systematically by Paul and Saint-Pierre a decade later [6], have remained unaddressed until very recently. Namely, positron-molecule annihilation rates exceed greatly those expected for simple, two-body collisions. While the effects were attributed to resonances from the very beginning, and many studies were conducted in the meantime, definitive confirmation of such a resonance picture has been very slow in coming. In our view, the key experimental ingredient was the development of a tunable-energy, high resolution positron beam capable of resolving structure associated with the molecular vibrational modes [7]. Using this new tool, annihilation-rate resonances were discovered that are associated with the molecular vibrational modes [8-14].

A typical resonance spectrum is shown in Fig. 1 for the six-carbon alkane, hexane. The normalized rate, Z_{eff}, shown there is the measured annihilation rate, λ, normalized to that for a free electron gas, specifically

$$Z_{eff} = \frac{\lambda}{\pi r_0^2 c n_m} , \qquad (1)$$

where r_0 is the classical electron radius, c is the speed of light, and n_m is the density of the target atoms or molecules. Thus the benchmark value $Z_{eff} = Z$, where Z is the number of electrons in the target, corresponds to annihilation in an uncorrelated electron gas with electron density $n = n_m Z$. However, below ~ 0.4 eV, giant enhancements are observed that are far larger than the expected free-electron value.

Note that the peaks in Fig. 1(a) correspond well to the spectrum of molecular vibrations in hexane, shown in the IR spectra in Fig. 1(b). The relatively isolated peak at ~280 meV is due to the asymmetric C-H stretch vibrational mode, which we will refer to in this paper as the C-H stretch peak. The spectrum at lower energies is due to C-C modes and C-H bend modes. The line shapes of the peaks are explained by the energy distribution of the positron beam, indicating that the resonances themselves are much narrower.

A key feature of the comparison of the Z_{eff} and IR spectra shown in Fig. 1 is the downshift of the former with respect to the latter. The Z_{eff} peaks are vibrational Feshbach resonances. Consequently, there is an energy downshift in the annihilation spectrum relative to that of

the molecular vibrational energies of magnitude

$$\Delta\varepsilon = \varepsilon_v - \varepsilon_v^{res} = \varepsilon_b, \qquad (2)$$

where ε_v^{res} is the position of the resonant peak associated with vibrational mode ν, ε_v is the vibrational-mode energy and ε_b is the positron-molecule binding energy. A general feature of the data for many molecules is that, while the shift, $\Delta\varepsilon$, varies from molecule to molecule, it is the same for all resonant modes within a given molecule.
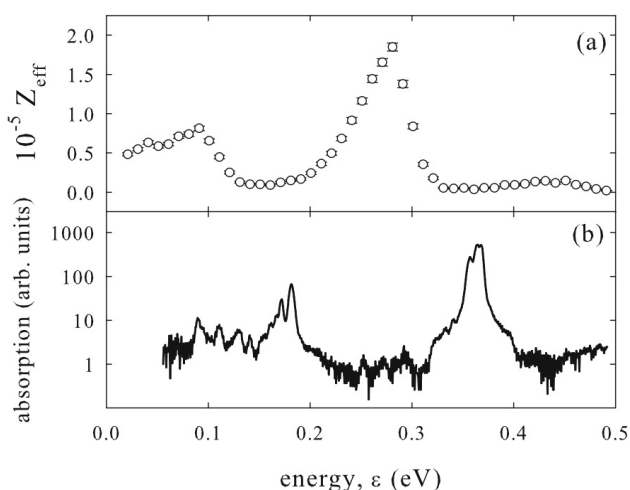
Figure 1 (a) The annihilation spectrum (expressed in terms of the dimensionless parameter, Z_{eff}), and (b) the infrared absorption spectrum (log scale, arbitrary units) for hexane. Note that, when the 80 meV downshift of the Z_{eff} spectrum due to the positron-hexane binding energy is taken into account, the strong peaks in the two spectra occur at the same energy. Reprinted from Ref. [13]; see this reference for details.

In practical terms, the key point is that such *Feshbach-resonant annihilation spectra can be used to measure positron-molecule binding energies*. It is critical to note that the very existence of these Feshbach resonances *requires* such a non-zero binding energy; thus these resonant spectra not only provide clear evidence that positrons bind to molecules, but they also provide quantitative measures of positron-molecule binding energies via Eq. (2). To date, binding energies for 30 molecules have been measured, ranging from a few millielectron Volts to > 0.3 eV [13, 14].

In this paper, we present a brief review of the subject of resonant annihilation on molecules, the important results that studies of this phenomenon have yielded, and a discussion of open questions for future research.

2 Experimental procedures The procedures used to measure annihilation rates resolved as a function of positron energy have been discussed in detail in a series of papers [8, 9, 11-14]. A schematic of the apparatus is shown in Fig. 2. Pulses of positrons from a trap-based cold positron beam are magnetically guided through the cylindrical

electrode of a cell filled with the test gas. The component of the positron energy in motion parallel to the magnetic field is obtained from retarding potential analyzer measurements (~ 25 meV, FWHM). This is in addition to the thermal (Maxwellian) energy distribution of the particles in motion in the plane perpendicular to the magnetic field, which also corresponds (by coincidence) to a temperature of 25 meV. Thus the resulting spread in total energy of the beam particles is ~ 50 meV, FWHM [10].

Typically, pulses of $\geq 10^4$ positrons are cycled through the cell at a 4 Hz rate. These pulses are kept in flight while the annihilation is monitored. They are made to transit the cell from one to four times, with the number of passes adjusted to obtain good signal to noise. Energy spectra for $Z_{eff}(\varepsilon)$ are plotted as a function of total incident positron energy, ε. Single quanta from two-gamma annihilation events are detected using a CsI detector.

The beam is magnetically guided, and the pressure in the region where annihilation is monitored can be measured accurately. As a consequence, absolute values of the annihilation rates can be obtained from measurements of the positron pulse strength, the path length, and the test-gas pressure. The resulting values of Z_{eff} can be determined to within an absolute accuracy of approximately 20%. As mentioned above, the widths and shapes of the observed resonances, such as those illustrated in Fig. 1, are dominated completely by the energy distribution of the incident positron beam.
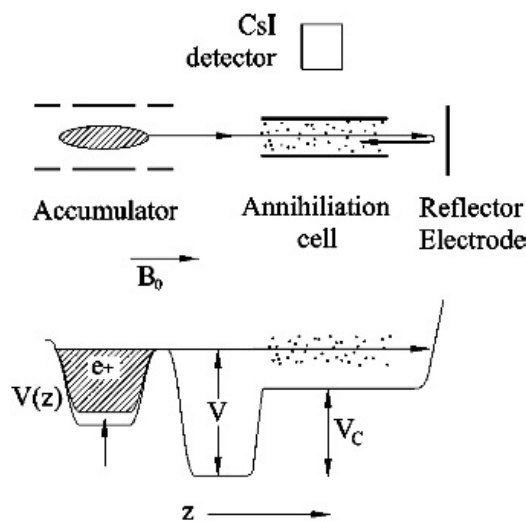

Figure 2 Schematic diagram of the experiment (above), and the corresponding electrical potential $V(z)$ as a function of position along the (z) direction of the magnetic field (below). Pulses of monoenergetic positrons are passed through the annihilation cell filled with the test gas. The energy of the beam can be tuned from 50 meV to several tens of electron Volts. Figure reprinted from Ref. [8]; see the text and this reference for details.

3 Annihilation in small molecules It has proven useful to separate the data for resonant annihilation on molecules into two classes, that for molecules with one or

two carbon atoms (which we call "small" molecules) and that for larger molecules. Gribakin and Lee have developed a successful theory of Feshbach-resonant positron annihilation for the case of small molecules [10] when the spectrum is dominated by isolates, individual vibrational resonances that are coupled to the positron continuum (e.g., by dipole coupling). According to this theory, the normalized annihilation rate, Z_{eff}, for the resonant process can be written as

$$Z_{eff}(\varepsilon) = \frac{2\pi}{r_o^2 c} \sum_{\upsilon} \frac{b_{\upsilon} \Gamma_{\upsilon}^a \Gamma_{\upsilon}^c}{k_{\upsilon} \Gamma_{\upsilon}} f(\varepsilon - \varepsilon_{\upsilon}^{res}), \qquad (3)$$

where b_{ν} is the multiplicity of vibrational mode ν, k_{ν} is the incident positron momentum at the energy of resonance ν, and Γ_{ν}^a, Γ_{ν}^c, and Γ_{ν} are respectively the annihilation width, the capture (and emission) width, and the total width; and $f(\varepsilon)$ is the energy distribution of the incident positron beam.
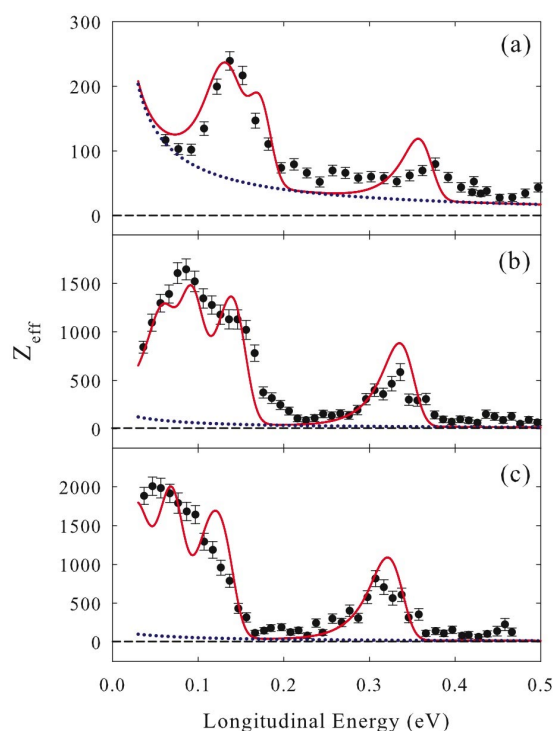
Figure 3 (Color online) Z_{eff} spectral data (•) compared with the Gribakin-Lee model (full curve) for (a) methyl fluoride, (b) methyl chloride, and (c) methyl bromide, using positron-molecule binding energies of 0.3, 25, and 40 meV, respectively [16]. The solid curves are the predictions of the model, with the dotted curves indicating the non-resonant (direct) contributions to Z_{eff}. From Ref. [14]; see the text and this reference for details.

The most precise test of this theory to date is annihilation in the 1-halomethanes, CH_3F, CH_3Cl, and CH_3Br, and their fully deuterated analogs [10, 14]. The energy spectra of Z_{eff} for the hydrogenated species are shown in Fig. 3. In these species, all of the vibrational modes are dipole-coupled to the incident positron continuum, and so the cap-

ture widths, Γ^c, can be calculated from the Born-dipole approximation or taken from infrared absorption measurements [10]. The rates Γ_{ν}^a, Γ_{ν}^c, and Γ_{ν} are all small compared with the energy distribution of the incident positron beam used in the studies described here. Thus the experimental peaks are resolution limited, and consequently, the peak heights of the resonances are actually much larger than those shown in the experimental Z_{eff} spectra.

For the case of the halomethanes and similar molecules, a huge simplification arises from the fact that $\Gamma_{\nu}^a << \Gamma_{\nu}^c$. Thus the factors Γ_{ν}^c and Γ_{ν} in Eq. (3) cancel. As a result, all of the parameters in Eq. (3) are known except for the positron-molecule binding energy, ε_b [10]. As illustrated in Fig. 1, this quantity can be determined from experiment by the downshift in the Z_{eff} spectrum relative to that of the vibrational modes. As shown in Fig. 3, there is agreement between the predictions of Eq. (3) and the measured values of Z_{eff}, both in magnitude of the peaks and in the spectral shapes, with only one adjustable parameter per spectrum, namely ε_b. Inspection of the fits in Fig. 3 indicate that the choices that best fit the amplitude of the spectra also fit well the positions of the C-H stretch peaks, particularly in CH_3Cl, and CH_3Br. This provides a strong validation of the theory.

The position of the C-H stretch peak in CH_3F is not currently understood. It occurs slightly above the position of the C-H vibrational mode, which would nominally indicate a negative binding energy. In contrast, the fact that resonances are observed, indicates that ε_b is positive. We have tentatively concluded that other factors are contributing to this upshift.

Recently, the theoretical model of Ref. [10] was tested further in the deuterated 1-halomethanes [12]. It is known from experiments on several molecules that the positron-molecule binding energy does not change with deuteration [9, 15]. Thus the values of the binding energy taken from the hydrogenated species can be used to provide *absolute* theoretical predictions for the case of the deuterated molecules. The results for CD_3Cl and CD_3Br (i.e., molecules for which ε_b is large enough to resolve in experiments on the hydrogenated analogs) show very good, absolute agreement between theory and experiment, in this case with *no* fitted parameters [12].

The major impediment to further progress with this formalism is that, ignoring degeneracy, the magnitudes of isolated resonances in this model are limited to $Z_{eff} \sim 10^3$ for the energy spread of the positron beam used in the experiments described here [16]. However, many larger molecules (particularly hydrocarbons; cf. Fig. 1) have Z_{eff} values that exceed this limit by orders of magnitude. This leads us to consider possible additional enhancement mechanisms that are discussed in the next section.

4 Annihilation in molecules with many vibrational modes In the alkane molecules (C_nH_{2n+2}), experiments show that Z_{eff} increases rapidly (*exponentially*) with molecular size. Generally, this trend is obeyed by all of the

larger hydrocarbons studied to date (e.g., alkanes with $n \geq 3$) and other species such as aromatic and partially fluorinated hydrocarbon molecules. An example of alkane molecules for which this is true are shown in Fig. 1, and two more examples are shown in Fig. 4. Since the peak values of Z_{eff} exceed greatly those predicted by the single-resonance theory of Eq. (3) (i.e., substantially in excess of $Z_{eff} = 10^3$), Gribakin has concluded that other phenomena must be involved [16].
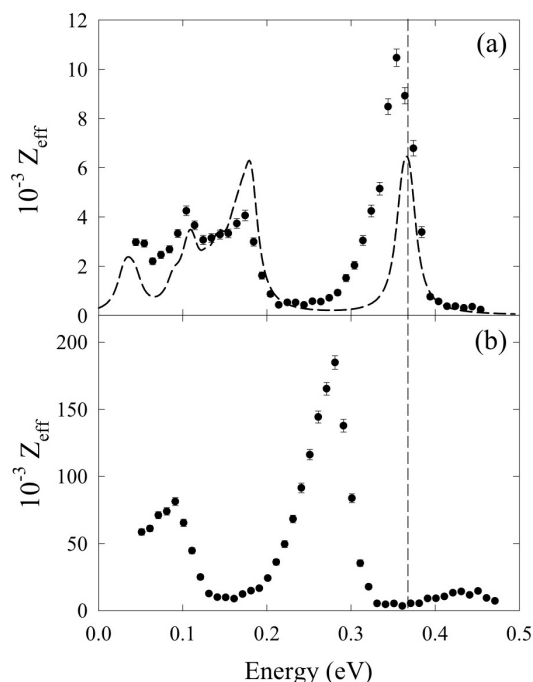
Figure 4 The energy-resolved Z_{eff} spectra for (a) propane, C_3H_8, and (b) hexane, C_6H_{14}, both scaled by a factor of 10^{-3}. Also shown in (a) is the vibrational mode spectrum for propane (---), arbitrarily scaled in amplitude and artificially broadened by a Lorentzian line shape with a width of 10 meV. The vertical dashed line indicates the position of the C-H stretch mode in these molecules. Figure reprinted from Ref. [8]; see the text and this reference for details.

While presently not confirmed directly to date, the following picture has emerged. In molecules with many modes, the positron can become attached via so-called "doorway" resonances (e.g., dipole-allowed vibrational transitions), and then these states couple to other, so called "dark states" (i.e., vibrational modes that are not themselves coupled to the positron continuum) [17] by the process known as intramolecular vibrational energy redistribution (IVR). These additional resonances, in turn, can increase greatly the amplitude of Z_{eff}. This arises from the fact that the number of accessible modes and mode combinations rises exponentially with molecular size. In this case, estimates of the density of dark states indicate that if, for example, in alkanes, all dark states were populated by coupling to a doorway state, a much larger increase of

Z_{eff} would be observed than is found in the experiments [17].
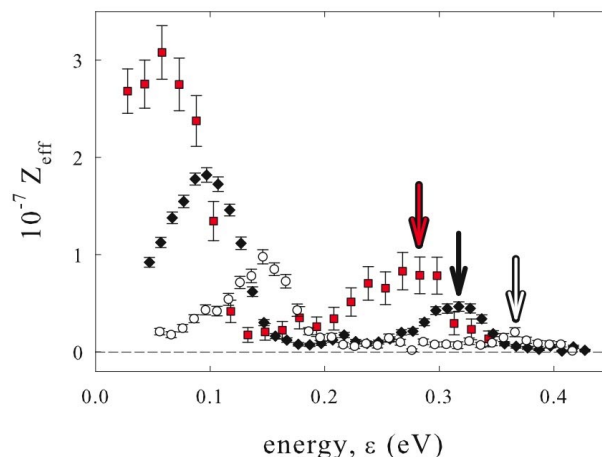
Figure 5 (Color online) Z_{eff} spectra for (open circles) dodecane ($C_{12}H_{26}$), (squares) tetradecane ($C_{14}H_{30}$), and (closed circles) hexadecane ($C_{16}H_{34}$). The vertical arrows indicate the positions of the C-H stretch mode VFR peaks for the second bound states (i.e., positronically excited states) in each molecule. The spectra for tetradecane and hexadecane have been arbitrarily normalized. The large peaks at lower energy are the C-H stretch mode VFR for the first bound states (i.e., the positronic ground states). From Ref. [13]; see this reference for details.

Another interesting feature of the annihilation resonance spectra in alkanes is shown in Fig. 5. In the spectra for very large alkanes, $C_{12}H_{26}$, $C_{14}H_{30}$ and $C_{16}H_{34}$, new peaks are evident. In this case, the downshifts are much smaller than those of the primary C-H stretch modes (e.g., ranging from zero to ~ 100 meV), while the primary peaks are characterized by downshifts ~ 300 meV. We identify these features as second (i.e., "positronically excited") bound states, mediated by excitation of the C-H stretch vibrational mode [13]. The fact that they appear in the larger alkane molecules is consistent with the predictions of a zero-range potential (ZRP) model for alkanes by Gribakin and Lee [18].

5 Dependence of Z_{eff} on binding energy and molecular size The theory of Gribakin and Lee for single resonances [i.e., as expressed by Eq. (3)] predicts that Z_{eff} should be proportional to $g = (\varepsilon_b/\varepsilon)^{1/2}$, where ε is the energy of the incident positron. While this theory was developed for the case of individual resonances, we recently considered it in the context of annihilation in larger molecules [11]. As shown in Fig. 6, when the scaling on g is normalized out of Z_{eff}, the resulting values lie close to a universal curve given by

$$Z_{eff}/g \propto N^{4.1}, \qquad (4)$$

where N is the number of atoms in the molecule [11, 13]. We interpret the dependence on N to indicate that Z_{eff} in-

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creases approximately as the fourth power of the *number of vibrational degrees of freedom*. A key observation relating to this analysis is that *there is no additional dependence of Z_{eff} on positron-molecule binding energy* beyond that represented by the factor g. We note that the observed rapid dependence of Z_{eff} on N agrees qualitatively with what one might expect if IVR coupling to dark states were important.
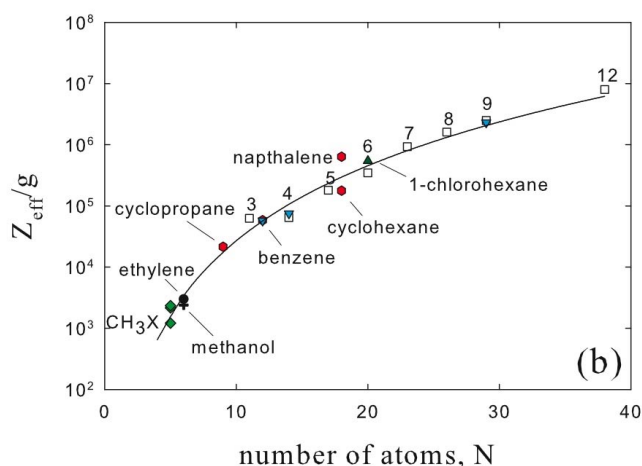
Figure 6 (Color online) Values for Z_{eff} at the C–H stretch peak, scaled by the factor $g = (\varepsilon_b/\varepsilon)^{1/2}$, as a function of the total number of atoms in the molecule, N (i.e., interpreted physically as the number of vibrational degrees of freedom) for various species. Alkanes (C_nH_{2n+2}), shown as open squares, are marked by the number, n, of carbon atoms in the chain. The solid line is a fit to the data of the form $Z_{eff} \propto N^{4.1}$. Reprinted from Ref. [11]; see Refs. [11, 13] for details.

A remarkable feature of the positronic ground-state and the first excited state C–H stretch resonances shown in Fig. 5 is that the ratios of the intensities of these peaks, relative to those of the C-H resonances for the positron ground state resonances, *also obey the g scaling*. We interpret this scaling with g, given by Eq. (4) and illustrated by the trend shown in Fig. 6, to indicate that inelastic escape channels are largely inactive [11, 13]. Namely, for shallow bound states, many more vibrational modes can inelastically de-excite and eject the bound positron than for states that are deeply bound. Thus the values of Z_{eff} are expected to be corresponding smaller for those states than could be accounted for by application of the g-factor scaling alone. *Our conclusion is that inelastic escape channels are generally inoperative.* However, we have developed evidence of an operative inelastic escape channel in the case of the partially fluorinated alkanes [13]. This is not unexpected since vibrational excitation measurements indicate that the positron couples very strongly to the C-F bond [19].

A paramount question remains in explaining the magnitudes of the very large Z_{eff} values that are observed in large molecules. If all of the positrons that attached to molecules and populated the dark states *were to remain at-tached* (e.g., occupying the available dark states statistically), then all Z_{eff} values would be approximately the same (i.e., discounting the fact that Z_{eff} would increase slowly with molecular size due to the increase in capture cross section). In fact, this is not what is observed; the annihilation rate, Z_{eff}, increases rapidly with molecular size for almost all of the species studied to date. While only a speculation at present, it may be that *quasielastic escape channels* provide the additional mechanism that causes Z_{eff} to vary as it does in these larger molecules. In particular, if the escape channel had an energy very close to that of the doorway state, its energy would exceed ε_b and thus sufficient to eject the positron into the positron continuum. However additional studies will be required to provide a conclusive answer to this question.

6 Positron–molecule binding energies on molecular properties We now have measurements of positron-molecule binding energies for approximately thirty compounds [13]. In addition, five other molecules appear to have positive binding energies (i.e., in that they exhibit Feshbach resonances), but ε_b is too small to measure. Examples for three chemical species are given in Table 1. They show a broad range of values. Examples are CH_3F, whose binding energy is tiny, and $C_{12}H_{26}$ which has a binding energy of 220 meV and a small feature indicating the appearance of a second (positronically excited) bound state. The ground-state binding energy of napthelene is even larger, but it has no second bound state.

Table 1 Positron binding energies (in meV) and Z_{eff} at the C-H stretch peak for selected molecules, with Z the number of molecular electrons. From top to bottom, shown are data for 1-fluoromethane and 1-bromomethane, four alkane molecules, and the two aromatic molecules, benzene and naphthalene. The notation "≥ 0" denotes non-zero binding energies too small to measure. Data from Refs. [9, 13].

Molecule	Z	ε_b	Z_{eff}
CH_3F	18	≥ 0	35
CH_3Br	44	40	820
C_2H_6	18	≥ 0	900
C_3H_8	26	10	10,500
C_6H_{14}	50	80	184,000
$C_{12}H_{26}$	98	220	9,800,000
C_6H_6	42	150	47,000
$C_{10}H_8$	68	300	1,240,000

Presently, there are accurate calculations for positron binding to atoms [20]. However, there has been (under-

standably) less progress in the more difficult area of posi-tron binding to molecules [21–23]. In our view, a key chal-lenge for both experimentalists and theorists is to find molecules for which positron-molecule binding energies can be predicted accurately and studied experimentally. Likely this will first occur in the case of relatively small molecules, where the theory is more tractable, and for molecules that have an appreciable vapor pressure at not too high a temperature, so that they can be studied experi-mentally.

Regarding the magnitudes of positron binding energies, we have recently come to reconsider the molecular parame-ters that determine their magnitudes. As shown in Fig. 7, molecular polarizability appears to be a very significant factor, but it also appears that permanent dipole moment and the number of π bonds on a molecule tend to increase positron-molecule binding energies as well [24].
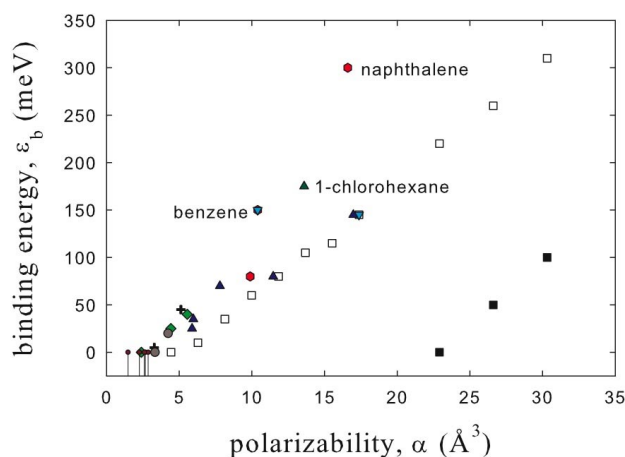
Figure 7 (Color online) Binding energy vs polarizability for a variety of molecules: alkanes (open squares); alkane second bound states (solid squares) rings (red hexagons): halomethanes (green diamonds); acetylene and ethylene (gray circles); alcohols (+), 1-chlorohexane (dark green triangle), fluoroalkanes (blue tri-angles) and deuterated species (cyan inverted triangles). VFR-weak or inactive species (small red circles) have a drop line to in-dicate possible "negative" binding energies (i.e., as virtual states). Figure reprinted from Ref. [13]; see this reference for details.

7 Concluding remarks In the past few years, much progress has been made in developing a quantitative un-derstanding of positron annihilation on molecules at ener-gies below the threshold for positronium formation. In many molecular species, there is strong evidence for Feshbach-resonance-mediated attachment. This, in turn, has provided *the* key evidence that positrons bind to mole-cules and measurements of binding energies. In the case where all of the vibrational modes are dipole-allowed, there is a successful *quantitative* theory of the resulting resonant annihilation rates.

While many, if not most molecules exhibit annihila-tion resonancs, particularly larger ones, some molecules, such as CH_4, H_2O and the perfluorinated alkanes (i.e., C_nF_{2n+2}), do not [13, 14]. We interpret this to mean that positrons do not bind to these molecules (i.e., $\varepsilon_b < 0$).

To date, positron-molecule binding energies have been measured for thirty species. Our experiments indicate that five more molecules are bound, but the magnitudes of their binding energies are too small to resolve. These data repre-sent the first experimental measurements of positron bind-ing energies to either atoms or molecules. While there are accurate calculations of positron binding to atoms [20], there are no experimental measurements of them. It is the presence of low-lying excitations in molecules (i.e., the molecular vibrational modes) that enables interrogation of the positron-molecule attached state via vibrational Feshbach resonances. Since atoms do not have such low-lying inelastic excitations, this kind of measurement is not possible.

For larger molecules, the mechanism that sets the magnitude of the annihilation rate is less clear. It is likely that the process of intramolecular vibrational energy redis-tribution (IVR) from doorway to dark states plays an im-portant role, however the details of this process have yet to be developed. Thus one very important area for future re-search is to develop a better understanding of the mecha-nism of Z_{eff} enhancement in large molecules. It appears that this will involve developing a better understanding of the extent to which IVR occurs in these species. For exam-ple, does IVR only occur for a certain fraction of the modes, and if so, which ones and how are they coupled to the doorway states?

A second critical area for future research is the need to make contact between theory and experiments on the magni-tudes of positron-molecule binding energies. As mentioned above, this will likely involve choosing test molecules par-ticularly carefully so as to be amenable to prediction using currently available theoretical techniques and also amenable to experimental study. In experiments such as those de-scribed here, the latter will require test species sufficiently large vapor pressures at not too high temperature (e.g., vapor pressures $\geq 10^{-5}$ Torr at temperatures ≤ 800 K).

Other interesting topics for future research include in-vestigating the consequences that resonant annihilation might have for positron-induced fragmentation of mole-cules [25–27] and study of the (likely resonant) process of positron annihilation in atomic clusters and similar species such as large polycyclic aromatic hydrocarbons (PAHs) [2].

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