

Resonant Positron Annihilation on Molecules

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Abstract. At incident positron energies below the threshold for positronium atom formation, there are many cases in which annihilation rates for molecules are far in excess of that possible 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. The attachment enhances greatly the overlap of the positron with molecular electrons and hence increases the probability of annihilation. Furthermore, measurements of the annihilation spectra as a function of incident positron energy provide a means of measuring positron-molecule binding energies. In this paper we present an overview of our current understanding of this process, highlighting key results and discussing outstanding issues that remain to be explained.

I. Introduction

One of the most basic interactions between matter and antimatter is the annihilation of low-energy positrons in interactions with atoms and molecules below the threshold for positronium formation. This is important in many areas of science and technology including astrophysics, medicine (e.g., positron emission tomography, PET), and materials science [1-6]. Remarkably, outstanding questions first raised in the seminal experiments by Paul and Saint Pierre in the 1960's [7] have remained unsolved until very recently. Namely, positron-molecule annihilation rates were found to exceed greatly those expected for simple, two-body collisions. While many experimental and theoretical studies have been conducted since those original experiments, it was only recently that one could study positron-molecule annihilation using positrons with a well-controlled and tunable energy sufficient to resolve structure on the scale of the molecular vibrational energies [8]. When this was done, huge resonances in annihilation rates were discovered that bear a close resemblance to the spectra of the molecular vibrations [9].

The example of annihilation in butane (C_4H_{10}) is shown in Fig. 1. Note the large enhancements in annihilation at energies below ~ 400 meV, which is the region of the molecular vibrations. The relatively isolated peak at ~ 330 meV is due to the asymmetric C-H stretch vibrational mode, which we refer to here at the C-H stretch peak. The spectrum at lower energies is due to C-C modes and C-H bend modes. The lineshape is explained completely by the energy spread of the positron beam, so the resonances are much narrower in energy than the peaks in the annihilation spectra.

These spectra have been interpreted successfully as due to vibrational Feshbach resonances. Furthermore, as illustrated in Fig. 1, the observed energy downshifts in the spectra relative to the molecular vibrational energies,

$$\Delta\mathcal{E} = \varepsilon_v - \varepsilon_b, \quad (1)$$

where ε_v is the vibrational mode energy and ε_b is the positron-molecule binding energy, provide a measure of the non-zero positron-molecule binding energy (i.e., a binding which is required for the existence of the vibrational Feshbach resonances). In the case of butane, shown in Fig. 1, $\varepsilon_b = 35$ meV. In this paper, we summarize our understanding of this phenomenon and present an overview

of the positron-molecule binding energies measured to date. We also discuss outstanding questions yet to be resolved.

II. Description of the Experiments

The procedures used to measure atomic and molecular annihilation rates as a function of positron energy have been discussed in detail elsewhere [9, 10]. A schematic of the experimental setup 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. Total positron energy is obtained from retarding potential analyzer measurements of the parallel energy distribution (25 meV, FWHM), assuming a thermal Maxwellian energy distribution in the plane perpendicular to the magnetic field with a temperature of 25 meV [11].

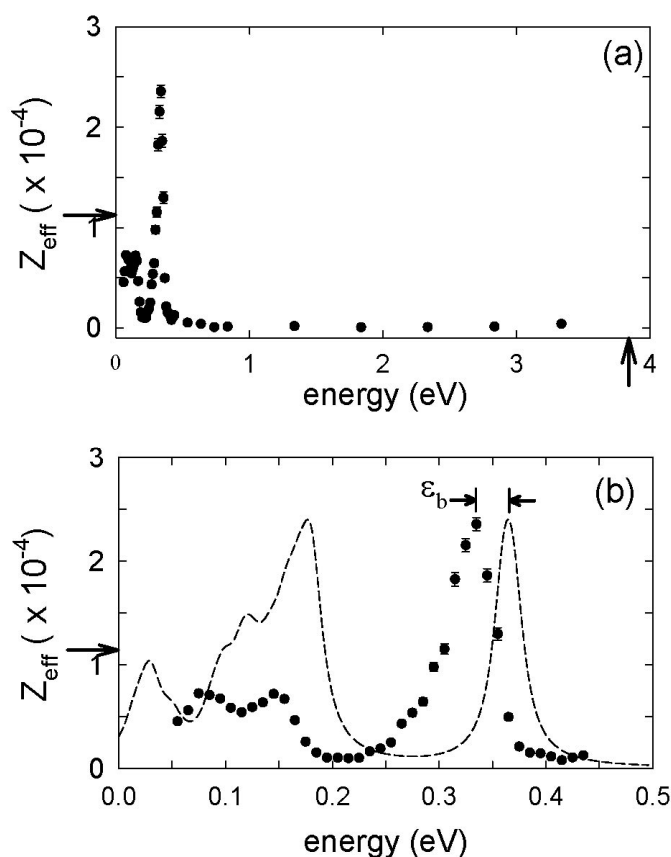


Figure 1. (a) annihilation spectrum of butane (C_4H_{10} ; ●) as a function of the total incident positron energy, ε , represented as the normalized quantity, Z_{eff} [defined in Eq. (2) below]; and (b) Z_{eff} on an expanded scale in the region of the molecular vibrations, with (---) the vibrational mode spectrum of butane (in arbitrary units) artificially broadened by 10 meV. The horizontal arrows indicate Z_{eff} for thermal positrons at 300 K. The vertical arrow in (a) shows the threshold for positronium formation in butane. Reprinted from Ref. [10].

Energy spectra for Z_{eff} , are plotted as a function of total incident positron energy, ε . 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. Single quanta from two-gamma annihilation events are detected using a CsI detector. Absolute values of the

annihilation rates are obtained from measurements of the positron pulse strength, the path length, and the test-gas pressure to within an absolute accuracy of approximately 20%.

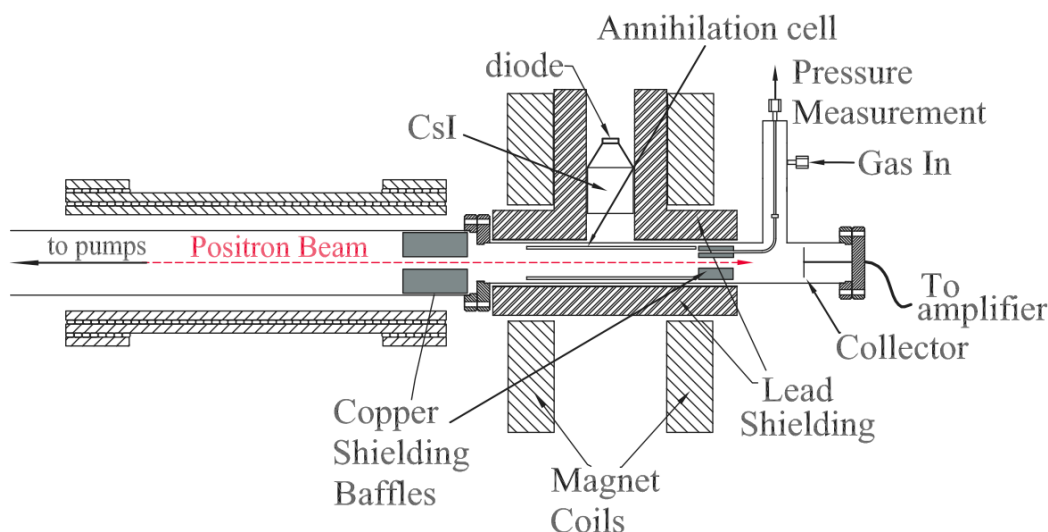


Figure 2. Schematic diagram of the experimental setup used to measure positron-molecule annihilation rates. The key features are a tunable, trap-based positron beam with a parallel energy spread ~ 25 meV, FWHM, and a similar perpendicular energy spread, and the fact that the beam is magnetically guided through the gas cell with a field ~ 0.08 tesla. From Ref. [12]. See text for details.

III. Prototypical Case of Small Molecules – Annihilation in 1-Halomethanes

Annihilation rates are typically expressed in terms of the quantity Z_{eff} , which is the annihilation rate, λ , normalized to that for a free electron gas, namely

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

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 condition $Z_{\text{eff}} = Z$, where Z is the number of electrons in the target, corresponds to annihilation in an uncorrelated electron gas with electron density $n = n_m Z$. This is, in fact, much smaller than the rates observed for many molecules interacting with low-energy positrons. In alkane molecules, for example, Z_{eff} can be $\sim 10^4 - 10^7$. Gribakin and Lee have developed a successful theory of Feshbach-resonant positron annihilation [11]. According to this theory, the normalized annihilation rate, Z_{eff} , for the resonant process can be written,

$$Z_{\text{eff}}(\epsilon) = \frac{2\pi}{r_0^2 c} \sum_v \frac{b_v \Gamma_v^a \Gamma_v^c}{k_v \Gamma_v} \Delta(\epsilon - \epsilon_v), \quad (3)$$

where b_v is the multiplicity of vibrational mode v , k_v is the incident positron momentum at the energy of resonance v , Γ_v^a , Γ_v^c , and Γ_v are respectively the annihilation width, the capture (and emission) width, and the total width; and $\Delta(\epsilon)$ is the energy distribution of the incident positron beam.

Thus far, the most precise test of this theory is annihilation in the 1-halomethanes, CH_3F , CH_3Cl , and CH_3Br , and their fully deuterated analogs. The energy spectrum of Z_{eff} for CH_3Br is shown in

Fig. 3. In this and other halomethanes, all of the vibrational modes are dipole coupled to the incident positron, and so the capture widths, I^e , can be calculated from the Born-dipole approximation or taken from infrared measurements [11]. Thus all of the parameters in Eq. (3) are known except for the binding energy, ε_b . As illustrated in Fig. 1, this quantity can be determined from experiment by measuring the downshift in the Z_{eff} spectrum relative to that of the vibrational modes. There is good 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. This provides a strong validation of the theory.

Recently, the model was tested further in the deuterated 1-halomethanes [13]. In this case, it is known from experiments on several molecules that the positron-molecule binding energy does not change with deuteration. Thus 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 experiment) show very good, absolute agreement between theory and experiment, in this case with *no* fitted parameters. The magnitudes of isolated resonances in this model are limited to $Z_{\text{eff}} \sim 10^3$, ignoring degeneracy. However, many larger molecules have been shown to exceed this limit by orders of magnitude (c.f., Fig 1). Thus there is more to the story, which we discuss in the next section.

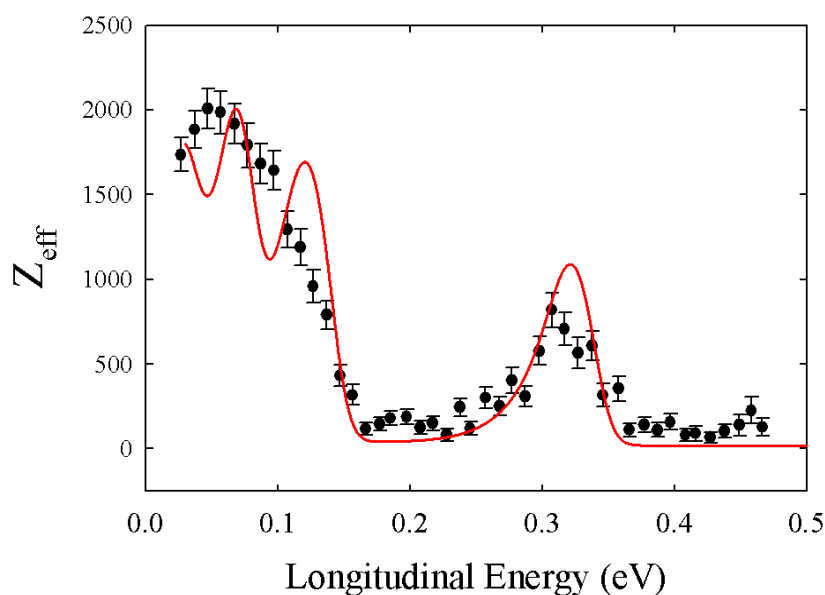


Fig. 3. Shown is the Z_{eff} spectrum for CH_3Br compared with the predictions of Eq. 3. In this case, the binding energy, ε_b is taken from the position of the C-H stretch peak. The resulting good agreement validates the theoretical predictions. Reprinted from Ref. [11].

IV. Annihilation in Larger Molecules and Evidence for Additional Enhancements

In simple hydrocarbon molecules such as the alkanes ($\text{C}_n\text{H}_{2n+2}$), experiments show that Z_{eff} increases *exponentially* with molecular size (i.e., with n), while the shift in the C-H stretch peak, which is a measure of the binding energy, increases linearly in proportion to n . Examples are shown in Fig. 4. Since the peak values exceed greatly those predicted by the single-resonance theory of Eq. (3) (i.e., $Z_{\text{eff}}/n > 10^3$), other phenomena must be involved. While presently unproven, it is believed that, in the case of larger molecules with many modes, the positron attaches to the molecule through so-called “doorway” resonances (e.g., dipole-allowed vibrational transitions), then these states couple to other, so called “dark” states that are not coupled to the positron continuum [14]. These added resonances, in turn, are believed to increase greatly the amplitude of Z_{eff} , due to 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 all were coupled to the doorway state, a much larger increase of Z_{eff} with n would be evident than that which is observed.

The theory of Gribakin predicts that Z_{eff} should be proportional to $g = (\epsilon_b/\epsilon)^{1/2}$, where ϵ is the energy of the incident positron. As shown in Fig. 5, when this scaling is normalized out of Z_{eff} , the values for many molecules lie on a universal curve,

$$Z_{\text{eff}}/g \propto N^{4.1}, \quad (3)$$

where N is the number of atoms in the molecule. We interpret this to mean that Z_{eff} increases approximately as the fourth power of the number of vibrational degrees of freedom. The key point is that no additional dependence of Z_{eff} on positron-molecule binding energy is observed beyond that represented by the factor g .

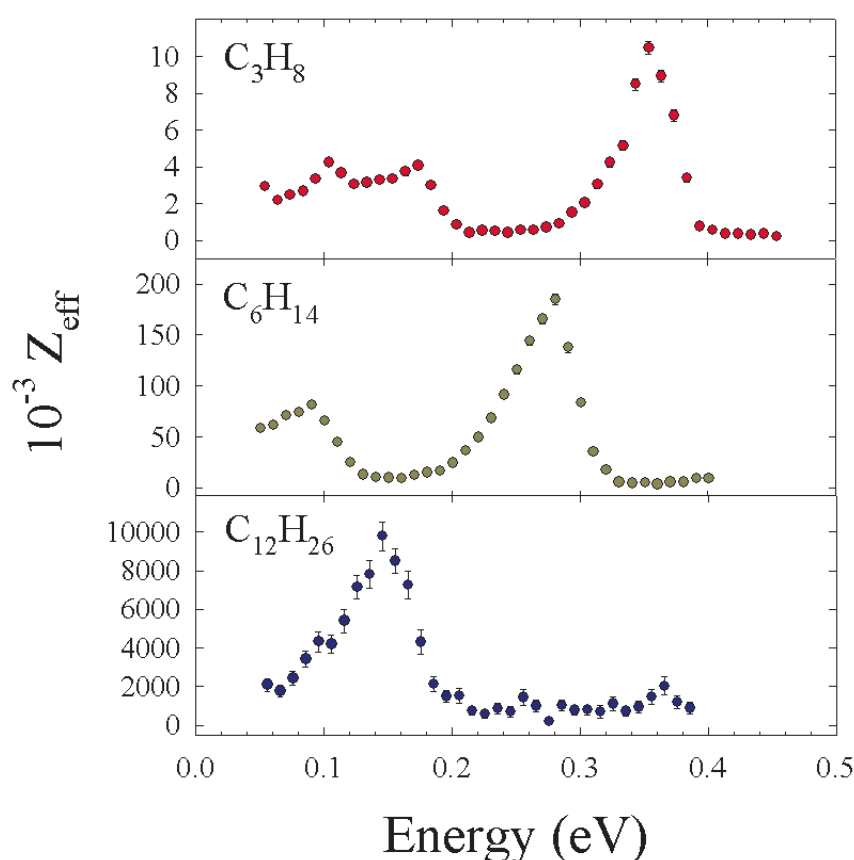


Fig. 4. Z_{eff} spectra for the selected alkane molecules, C_4H_{10} , C_9H_{20} and $\text{C}_{12}\text{H}_{26}$. The large peak is the C-H stretch mode which has an energy $\epsilon_v \approx 370$ meV. Note the large increase in Z_{eff} with molecular size going from C_4H_{10} and C_{12}H_2 . This rapid increase with molecular size is common to all of the alkane measurements. Data from Refs. [10, 15].

In the spectra for $\text{C}_{14}\text{H}_{30}$ and $\text{C}_{16}\text{H}_{34}$, peaks downshifted by 50 and 100 meV, respectively, have been identified as second (i.e., “positronically excited”) bound states, mediated by excitation of the C-H stretch vibrational mode [16]. The intensities of these peaks, relative to those of the C-H stretch resonances for the positron ground states, also obey the g scaling. This scaling with g indicates that inelastic escape channels are generally inoperative [15, 16]. Namely, for more shallowly bound states, more modes could eject the bound positron, and the values of Z_{eff} would be lower than that which is observed. This contradicts the data, so we conclude that inelastic escape channels are generally inoperative. We note for completeness that there is, in fact, evidence of an operative

inelastic escape channel – the case of the partially fluorinated alkanes [16]. This is not unexpected since vibrational excitation measurements indicate that the positron couples very strongly to the C-F bond [17].

At least one key open question remains in explaining 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 *remained attached* (e.g., occupying the available dark states statistically), then Z_{eff} values would actually be roughly comparable (or at least Z_{eff} would increase only slowly as a function of molecular size) for the wide variety of molecules studied. This again contradicts the data. This is the limit of our present understanding. We hypothesize that quasielastic escape channels could be the mechanism that controls Z_{eff} , but this has yet to be verified.

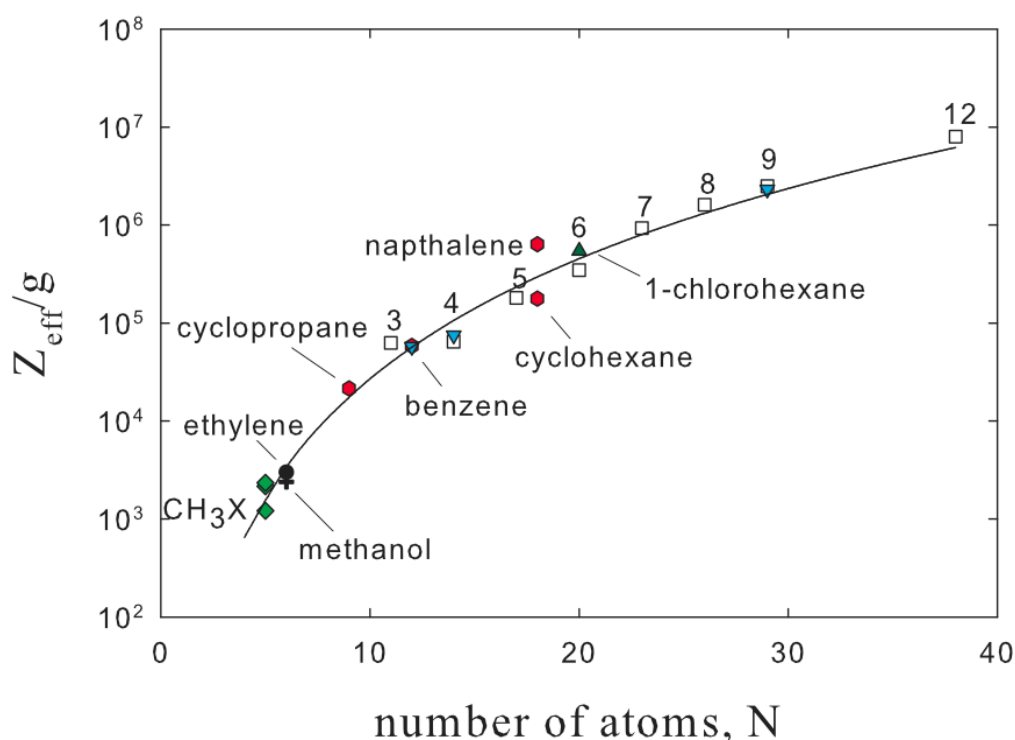


Fig. 5. Values for Z_{eff} at the C-H stretch peak, scaled by the factor $g = (\epsilon_b/\epsilon)^{1/2}$, as a function of the total number of atoms in the molecule, N (i.e., interpreted physically as the number of vibrational degrees of freedom) for various species. Alkanes ($\text{C}_n\text{H}_{2n+2}$), 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 $Z_{\text{eff}} \propto N^{4.1}$. From Ref. [15].

V. Positron-molecule Binding Energies

Through experiments such as those described above, we now have measurements of positron-molecule binding energies for approximately thirty compounds [16]. Another five or so are known to have positive binding energies (i.e., since they exhibit Feshbach resonances), but ϵ_b is too small to measure. Examples given in Table I show a broad range of values, from C_2H_6 and CH_3F , whose binding energies are too small to resolve accurately to $\text{C}_{16}\text{H}_{34}$ which has a binding energy of 310 meV and a second (positronically excited) bound state. The ground-state binding energy of naphthalene is similar, but it has no second bound state.

Table I. Positron binding energies (in meV) and Z_{eff} at the C-H stretch peak for selected molecules, with N and Z the numbers of atoms and molecular electrons, respectively. The notation “ ≥ 0 ” denotes non-zero binding energies too small to measure. Only relative Z_{eff} values are available for hexadecane, which is indicated by the arbitrary factor ‘x.’ Data from Refs. [16, 18].

Molecule	Formula	N	Z	ϵ_b	Z_{eff}
1-fluoromethane	CH ₃ F	5	18	≥ 0	35
1-bromomethane	CH ₃ Br	5	44	40	820
ethane	C ₂ H ₆	8	18	≥ 0	900
butane	C ₄ H ₁₀	14	34	35	21,000
octane	C ₈ H ₂₀	26	66	115	1,090,000
dodecane	C ₁₂ H ₂₆	38	98	220	9,800,000
hexadecane	C ₁₆ H ₃₄	50	130	310	15x
2 nd bound state				100	4x
benzene	C ₆ H ₆	12	42	150	47,000

VI. Concluding Remarks

Much progress has been made in understanding positron annihilation on molecules at energies below the threshold for positronium formation. There is strong evidence for Feshbach-resonance-mediated attachment. In the case where all modes are dipole-allowed, there is a successful quantitative theory of the resulting annihilation rates. For larger molecules, the picture is less clear. It is likely that intramolecular vibrational energy redistribution (IVR) plays an important role, but at a minimum, the details of this process are lacking.

These experiments highlight the importance of positron binding. While there are accurate calculations for positron binding to atoms [19], there has been less work in the area of positron binding to molecules [20-22]. A key challenge 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 ones that have an appreciable vapor pressure at not too high a temperature, so that they can be studied experimentally.

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