

Role of Binding Energy in Feshbach-Resonant Positron-Molecule Annihilation

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Measurements of positron-on-molecule annihilation have established that positrons bind to a variety of molecules via vibrational Feshbach resonances. Data for deeply bound states in benzene and 1-chlorohexane and for positronically excited (i.e., second) bound states in alkanes are used to establish the dependence of annihilation rates on the binding energy and incident positron energy. With this dependence removed, annihilation rates for a broad class of molecules lie on a universal curve as a function of the number of molecular vibrational degrees of freedom. The implications of these results for theoretical models are discussed.

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There are many interesting and important phenomena associated with low-energy electron and positron interactions with molecules and clusters [1,2]. One long-standing question is the origin of the large annihilation rates observed in positron-molecule interactions [2–7]. It is now clear that positrons can form temporary bound states with free molecules via vibrational Feshbach resonances (VFR) [7–9]. This process results in substantially enhanced rates of annihilation occurring at positron energies $\epsilon = \epsilon_\nu - \epsilon_b$, where ϵ_ν is the energy of a vibrational mode and $\epsilon_b > 0$ is the positron-molecule binding energy.

Annihilation rates are typically expressed in terms of Z_{eff} , which is the ratio of the annihilation rate λ for a given density of molecules n_m to the rate for the same density of free electrons. Specifically, $Z_{\text{eff}} = \lambda / (\pi r_0^2 c n_m)$, where c is the speed of light and r_0 is the classical electron radius. A simple scattering picture would suggest $Z_{\text{eff}} \lesssim Z$, the total electronic charge on the molecule [3,5–7]. However, for many molecules $Z_{\text{eff}} \gg Z$ because of VFR-mediated binding. For small molecules such as methyl halides, there is now quantitative agreement between a relatively simple theory of resonant annihilation and the results of experiments [10]. For larger molecules (e.g., hydrocarbons with two or more carbon atoms), the picture is less clear. In these molecules, Z_{eff} grows by orders of magnitude with increasing molecular size [9,11]. The binding energy ϵ_b also grows, but more slowly [9]. While it is uncertain how these parameters are related, it seems likely that intramolecular vibrational redistribution (IVR) is involved [12].

In this Letter, we focus on annihilation in these larger molecules. New data for positronically excited (i.e., second) bound states in large alkane molecules (hydrocarbon chains of the form $C_n H_{2n+2}$), and for the deeply bound species benzene and 1-chlorohexane, are used to determine the dependence of Z_{eff} on ϵ and ϵ_b . A simple theoretical energy scaling, tested recently for methyl halides, is found to work well for the larger molecules. With this dependence removed, the resulting normalized annihilation rates for a broad range of molecules lie on a universal curve as a function of the number of vibrational degrees of freedom. This result is potentially a great simplification for theories

of the annihilation process. In particular, it provides evidence that both inelastic escape channels and molecular structure have little effect on Z_{eff} .

According to a recent theory of resonant annihilation [7,12],

$$Z_{\text{eff}} = \frac{2\pi^2 \rho_{\text{ep}}}{k} \frac{\Gamma^{(e)}(\epsilon)}{\Gamma(\epsilon)} \rho(\epsilon + \epsilon_b), \quad (1)$$

where $k \propto \sqrt{\epsilon}$ is the positron momentum, ρ_{ep} is the electron-positron contact density in the bound state, $\Gamma^{(e)}$ is the elastic (i.e., capture) width, Γ is the total resonance width at positron energy ϵ , and $\rho(\epsilon + \epsilon_b)$ is the density of accessible vibrational states. Theory and experiment indicate that ϵ_b is the same for all modes of a molecule [7,9]. Using a simple *s*-wave model of the positron wave function at each center in the molecule, $\rho_{\text{ep}} \propto \sqrt{\epsilon_b}$. In this case, the explicit dependence of Z_{eff} magnitude on ϵ and ϵ_b is given by a simple scale factor, $g = \sqrt{\epsilon_b/\epsilon}$. Beyond this factor, Z_{eff} involves the unique dynamics between the positron, nuclei, and electrons. A key result of this Letter is that the factor g describes completely the dependence of resonant Z_{eff} on ϵ and ϵ_b for a broad range of large molecules.

The experimental procedures used to measure molecular annihilation rates as a function of positron energy are discussed in detail in Refs. [8,9,13]. Moderated positrons are accumulated and cooled in a three-stage buffer-gas trap. Pulses of positrons are then magnetically guided through the cylindrical electrode of a cell filled with the test gas. Incident positron energies are adjusted by varying the electrical potential of this cell. Total positron energy is obtained from retarding potential analyzer measurements, assuming a Maxwellian perpendicular energy distribution [10]. This results in a 4 meV reduction in energy as compared to the correction procedure used previously (e.g., in Refs. [9,13,14]). Energy spectra of Z_{eff} are plotted as a function of total positron energy, ϵ . Two-gamma annihilation events are detected using a single CsI detector. Typically, the positron pulses are allowed to pass through the gas cell 4 or 5 times while annihilation events are recorded, with total scattering kept below 15%. Absolute

values of Z_{eff} are obtained from measurements of the pulse strength, the path length, and the test-gas pressure. Uncertainties in these parameters are estimated to result in a 20% overall uncertainty in the absolute magnitude of Z_{eff} .

Shown in Fig. 1 is the energy-resolved annihilation rate, $Z_{\text{eff}}(\epsilon)$, for hexane (C_6H_{14}) [9]. Like other alkanes, hexane has large annihilation resonances associated with its fundamental vibrational modes. The dominant peak at $\epsilon \sim 280$ meV is due to excitation of the C-H stretch vibrational mode and so is referred to as the ‘‘C-H stretch peak.’’ It is downshifted below the mode by 80 meV because of the positron-molecule binding. The shape of the peak is entirely due to the energy spread of the trap-based positron beam [10]. The enhancement of the spectrum at energies $\epsilon \leq 0.13$ eV is due to VFR from other vibrational modes.

As the size of the alkane is increased, the C-H stretch peak moves to lower energy. Shown in Fig. 2 are data for the three largest alkane molecules measured to date, $\text{C}_{12}\text{H}_{26}$, $\text{C}_{14}\text{H}_{30}$, and $\text{C}_{16}\text{H}_{34}$. A new feature appears at ~ 370 meV in $\text{C}_{12}\text{H}_{26}$ and then moves to lower energy in sync with the C-H stretch peak as the size of the alkane is increased. These features in the spectrum are evidence of a second (i.e., positronically excited) bound state associated with the C-H stretch peak [15]. For the two largest molecules in Fig. 2, the absolute pressure in the annihilation cell was uncertain, so only the relative values of Z_{eff} within each spectrum can be determined. The heights and positions of the first and second bound state C-H stretch peaks were used to test the theoretically predicted scaling $Z_{\text{eff}} \propto g = \sqrt{\epsilon_b/\epsilon}$. As shown in Table I, Z_{eff}/g for the ground and first excited state peaks is identical in both $\text{C}_{14}\text{H}_{30}$ and $\text{C}_{16}\text{H}_{34}$ [16]. Since the changes in ϵ_b and ϵ are nontrivial, this is a strong confirmation of the proposed scaling.

Given the success of this scaling for peaks in the same large molecules, we were motivated to compare the heights of resonances in different molecules. Shown in Fig. 3 is the

energy-resolved annihilation spectrum of benzene as well as the locations of its vibrational modes from Ref. [17]. A broad background present in a previous measurement [13] was eliminated by lowering the transport energy to prevent false signals due to positronium formation outside the gas cell. This spectrum shows an unexpected feature at an incident positron energy, $\epsilon \sim 230$ meV. In particular, the C-H stretch modes, which produce the dominant resonances in most hydrocarbons, occur at ~ 380 meV in benzene. Associating the C-H modes with this benzene peak would imply a positron binding energy of 150 meV, which is much larger than the value of 80 meV for the six-carbon alkane, hexane. To verify the identity of this peak, the annihilation spectrum of fully deuterated benzene (benzene-d6) was measured. Since deuterated and non-deuterated species have the same electronic ground states, it is expected (and confirmed for a number of molecules) that they have the same binding energy [8,9].

The Z_{eff} spectrum for benzene-d6 is shown in Fig. 3. Comparison of the benzene and benzene-d6 spectra indicates that the large peak is indeed due to the C-H stretch mode and that $\epsilon_b \sim 150$ meV. In particular, after correcting for binding, the ratio of the C-H and C-D stretch peak energies is 1.28, which is close to the expected ratio of 1.34. The dashed line in Fig. 3 shows benzene-d6 with $\epsilon + \epsilon_b$ rescaled by 1.28 and Z_{eff} rescaled by the ratio of g factors. The adjusted spectrum is strikingly similar in magnitude and shape to that of benzene. This provides evidence that the scaling $Z_{\text{eff}} \propto g$ even works when comparing two different molecules.

The Z_{eff} spectrum for 1-chlorohexane is shown in Fig. 1. The binding energy, $\epsilon_b \sim 175$ meV, and C-H stretch peak height of this molecule are substantially larger than those of hexane, even though the number of atoms is the same, and the number of valence electrons is similar. When the

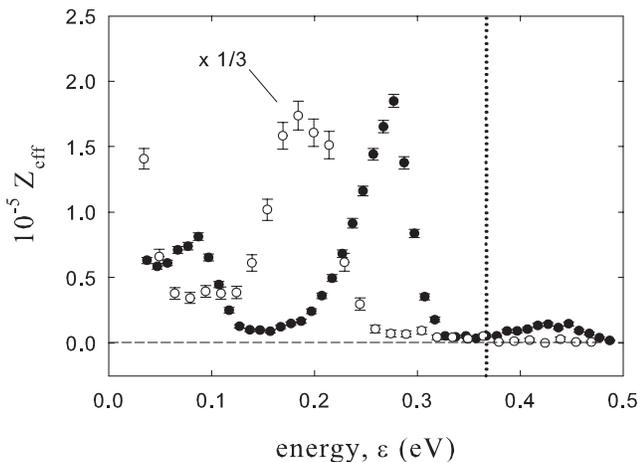


FIG. 1. Z_{eff} spectra for (●) hexane [9] and (○) 1-chlorohexane scaled by 1/3. The vertical dotted line represents the approximate energy of the C-H stretch vibrational mode. Note the large increase in binding energy and Z_{eff} in the chlorinated compound.

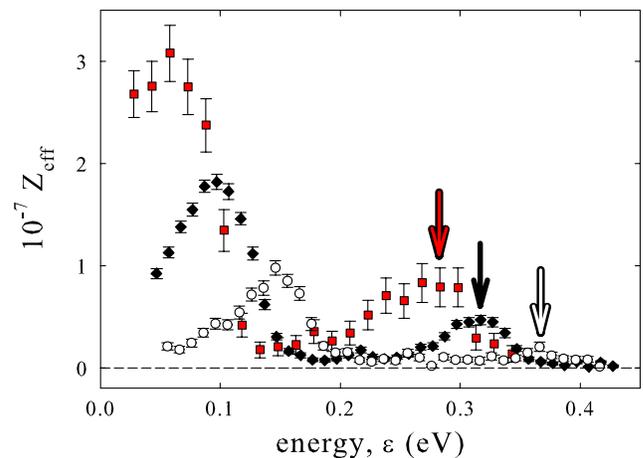


FIG. 2 (color online). Z_{eff} spectra for the large alkanes (○) $\text{C}_{12}\text{H}_{26}$, (◇) $\text{C}_{14}\text{H}_{30}$, and (□) $\text{C}_{16}\text{H}_{34}$. The smaller two molecules are from Ref. [13]. Data for $\text{C}_{14}\text{H}_{30}$ and $\text{C}_{16}\text{H}_{34}$ have arbitrary normalization due to an uncertainty in the absolute pressure. Vertical arrows indicate positions of the second bound state C-H stretch peaks.

TABLE I. Normalized C-H stretch peak values, Z_{eff}/g , for various molecules. The number of atoms per molecule N is provided for comparison.

Species	N	ϵ_b [meV]	Z_{eff}	Z_{eff}/g
methyl fluoride (CH ₃ F) ^b	5	0.3 ^c	35	1200
methyl chloride (CH ₃ Cl) ^b	5	25	585	2100
methyl bromide (CH ₃ Br) ^b	5	40	820	2300
cyclopropane (C ₃ H ₆) ^b	9	10	3600	21 500
propane (C ₃ H ₈) ^b	11	10	10 500	63 000
benzene (C ₆ H ₆) ^a	12	150	47 000	58 000
benzene-d6 (C ₆ D ₆) ^a	12	150	61 000	57 500
pentane (C ₅ H ₁₂) ^b	17	60	80 000	180 000
cyclohexane (C ₆ H ₁₂) ^b	18	80	94 000	180 000
hexane (C ₆ H ₁₄) ^b	20	80	180 000	340 000
1-fluorohexane (C ₆ H ₁₃ F) ^b	20	80	7000	13 200
1-chlorohexane (C ₆ H ₁₃ Cl) ^a	20	175	5.2×10^5	5.4×10^5
nonane (C ₉ H ₂₀) ^b	29	145	3.0×10^6	3.7×10^6
1-fluorononane (C ₉ H ₁₉ F) ^b	29	145	9.3×10^5	1.15×10^6
dodecane (C ₁₂ H ₂₆) ^b	38	220	9.8×10^6	7.8×10^6
tetradecane (C ₁₄ H ₃₀) ^b	44	260	11x	6.8x
2nd B.S.	44	50	2.8x	7.0x
hexadecane (C ₁₆ H ₃₄) ^a	50	310	15y	6.4y
2nd B.S.	50	100	4.0y	6.5y

^aPresent work.^bPrevious experiments [8,9,13].^cA theoretical prediction [10]. Absolute Z_{eff} for C₁₄H₃₀ and C₁₆H₃₄ are unknown, so values are multiplied by common factors “x” and “y.”

predicted scaling of Z_{eff} with g is taken into account, the ratio of the C-H stretch peak heights in 1-chlorohexane and hexane, while not unity, is reduced from 2.8 to 1.6 (cf. Table I).

Figure 4(a) shows Z_{eff} at the C-H stretch peak vs binding energy for alkanes and other species including 1-chlorohexane and benzene. While Z_{eff} typically increases

with ϵ_b (c.f., the alkanes), a number of molecules depart from this trend. As an alternative scaling, Fig. 4(b) shows Z_{eff} normalized by $1/g$ vs the number of atoms N , which removes these discrepancies. Unnormalized and normalized values of Z_{eff} for a variety of species are compared in Table I. Figure 4(b) and Table I indicate that hydrocarbons with a similar number of atoms tend to have similar normalized C-H stretch peak heights. These data can be fit empirically by a power law, $Z_{\text{eff}}/g = 2.3N^{4.07}$, where N is the number of atoms [c.f., solid line in Fig. 4(b)].

The major exception to this trend is the fluorine-substituted compounds such as 1-fluorohexane and 1-fluorononane [9,13], where the addition of a fluorine reduces Z_{eff} by a factor ~ 3 or more (cf. Table I), but leaves the binding energy unchanged. Recent results indicate that these molecules have a strong inelastic escape channel [18], thereby decreasing Z_{eff} . This is likely due to the C-F stretch mode, which has an unusually large vibrational coupling [19].

The fact that Z_{eff}/g depends so strongly on N (or alternatively, the number of vibrational degrees of free-

dom of the molecule, $3N - 6$) has interesting implications. It has been suggested that the rapid growth of Z_{eff} is due to the fact that single-mode vibrational resonances act as “doorways” [12], whose energy may be transferred into a large reservoir of higher-order, multi-mode vibrational excitations. This is thought to result in an enhancement of Z_{eff} roughly proportional to the

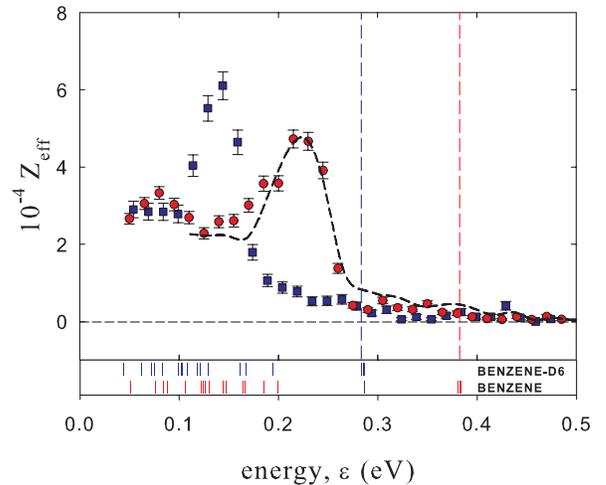


FIG. 3 (color online). Z_{eff} spectra for (○) benzene and (□) benzene-d6. The dashed line represents benzene-d6 spectrum with the derived mode energy, $\epsilon_v = \epsilon - \epsilon_b$, scaled by 1.28, assuming a binding energy of 150 meV, and the height scaled by 0.78. The lower panel indicates the positions of the vibrational modes in benzene and benzene-d6 from Ref. [17].

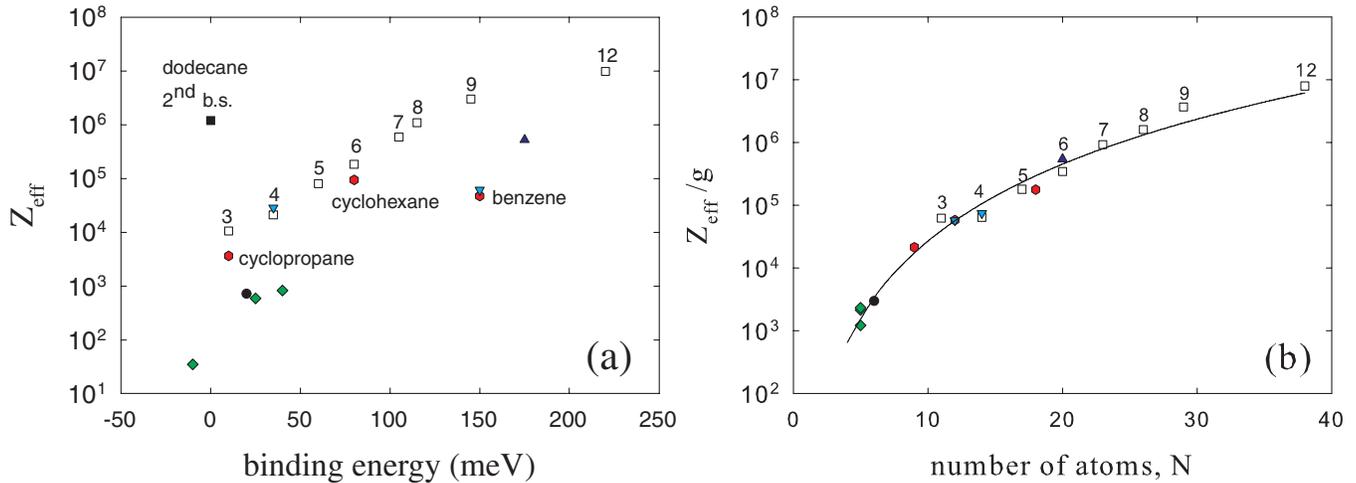


FIG. 4 (color online). (a) Z_{eff} at the C-H stretch peak vs binding energy for alkanes, C_nH_{2n+2} (\square); rings (red hexagons); halomethanes (\diamond); ethylene (\bullet); 1-chlorohexane (\triangle); and deuterated species (∇). (b) Z_{eff} at the C-H stretch peak normalized by the factor $g = \sqrt{\epsilon_b/\epsilon}$ vs the number of atoms in the molecule. For alkanes, the number of carbon atoms, n is indicated. The solid line shows the fit described in the text, $Z_{\text{eff}}/g = 2.3N^{4.07}$. This plot demonstrates that Z_{eff} is insensitive to positron binding beyond the weak dependence, g , which is predicted by theory.

local density of states, which in turn is expected to grow exponentially with N . While experiments show that the growth of Z_{eff} is not proportional to the total vibrational spectrum density as this simple model would predict [12], the fact that Z_{eff} does grow rapidly with N does suggest that intermolecular vibrational energy transfer (IVR) is important.

The lack of dependence of Z_{eff} on ϵ_b beyond the factor g is particularly interesting in this regard. A bound positron cannot escape via the deexcitation of a lower energy mode if the energy of the mode $\epsilon_v < \epsilon_b$. Thus, increasing ϵ_b should block escape *via* these inelastic channels, resulting in an additional enhancement in Z_{eff} and a deviation from the “universal” curve shown in Fig. 4(b). However, the only major outliers to this curve are the fluoroalkanes, likely due to a strong C-F stretch inelastic channel. Therefore, we conclude that only inelastic channels with very little positron energy loss can be active in most molecules.

In summary, large annihilation rates in molecules have only a relatively weak dependence on positron-molecule binding energies that is well described by the factor g . This provides evidence that inelastic escape channels are relatively unimportant. The most important parameter appears to be the number of vibrational degrees of freedom, indicating that details of molecular structure are relatively unimportant in determining resonantly enhanced values of Z_{eff} . Further studies of other nonalkane hydrocarbons as well as additional (e.g., second) bound states can be expected to clarify further the role of IVR in determining Z_{eff} .

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