



# The role of vibrational doorway states in positron annihilation with large molecules

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## Abstract

Positron annihilation rates in many polyatomic molecular gases are anomalously high. Qualitatively, this can be explained by positron capture in vibrational Feshbach resonances, which can occur for molecules with positive positron affinities [Gribakin, Phys. Rev. A 61 (2000) 022720]. To verify this idea quantitatively, we examine the densities of vibrational excitation spectra of alkanes. To understand the energy dependence of the annihilation rates for alkanes, we propose that positron capture is mediated by vibrational doorway states, in which positron binding is accompanied by the excitation of fundamentals.

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## 1. Introduction

In many polyatomic molecular gases room-temperature values of  $Z_{\text{eff}}$ , the effective number of electrons which contribute to the annihilation, exceed the number of electrons  $Z$  by many orders of magnitude [1–5]. At present, the only mechanism which can explain this phenomenon involves capture of positrons in vibrational Feshbach resonances (VFR) [6,7]. This mechanism is operational for molecules with positive positron affinities, and the corresponding  $Z_{\text{eff}}$  is proportional to the energy density of VFR.

Recently the San Diego group measured annihilation with a positron beam at high resolution (25 meV) [8,9]. For alkanes the peaks in the energy dependence of  $Z_{\text{eff}}$  match the spectrum of fundamentals with a downshift, which provides an evidence of binding. On the other hand, a dense spectrum of combination resonances and overtones is required to explain high  $Z_{\text{eff}}$  values [6,7]. The two points can be reconciled if one assumes that the positron is first captured in a quasi-bound “doorway” state, where a single vibrational mode is excited, which then spreads into complex VFR.

In this paper we evaluate the densities of VFR and compare them against experimental  $Z_{\text{eff}}$  at room temperature. Here we look at the dependence of thermal  $Z_{\text{eff}}$  on the size of the molecule. In order to understand the energy dependence of  $Z_{\text{eff}}$ , a model of vibrational doorways is developed and compared with experiment.

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## 2. Resonant contribution to $Z_{\text{eff}}$

Positron virtual states [10] and resonances [11,12] enhance annihilation. Using Breit–Wigner theory [13], we write the annihilation cross section for the  $s$  wave positron as a sum over the resonances,

$$\sigma_a = \frac{\pi}{k^2} \sum_v \frac{\Gamma_v^{(a)} \Gamma_v^{(e)}}{(\varepsilon - \varepsilon_v)^2 + \frac{1}{4} \Gamma_v^2}, \quad (1)$$

where  $k$  and  $\varepsilon = k^2/2$  are the positron momentum and energy (atomic units are used throughout),  $\Gamma_v^{(a)}$  is the annihilation width of state  $v$ ,  $\Gamma_v^{(e)}$  is its width with respect to re-emission of the positron,  $\Gamma_v$  is the total width,  $\Gamma_v = \Gamma_v^{(a)} + \Gamma_v^{(e)} + \sum_{E_v < \varepsilon} \Gamma_v^{(v)}$ , and  $\Gamma_v^{(v)}$  is the width of positron re-emission accompanied by vibrational excitation of the target with energy  $E_v$ . Positions of the resonances are given by  $\varepsilon_v = E'_v - |\varepsilon_0|$ , where  $\varepsilon_0 < 0$  is the positron–molecule bound state energy relative to threshold, and  $E'_v$  is the vibrational excitation energy of the complex ( $E'_v \approx E_v$ ).

## 3. Energy averaging

Closely spaced resonances cannot be resolved experimentally (thermal  $\Delta\varepsilon \sim 25$  meV), so (1) can be averaged over an energy interval  $\Delta\varepsilon \gg \varepsilon_{v+1} - \varepsilon_v$  [6,7],

$$\bar{\sigma}_a = \frac{2\pi^2}{k^2} \frac{\Gamma^{(a)} \Gamma^{(e)}(\varepsilon)}{\Gamma(\varepsilon)} \rho(\varepsilon + |\varepsilon_0|), \quad (2)$$

where  $\Gamma^{(e)}(\varepsilon)$  and  $\Gamma(\varepsilon)$  are the average widths at energy  $\varepsilon$  and  $\rho(\varepsilon + |\varepsilon_0|)$  is the level density of the positron–molecule vibrational excitations. Using

$$\bar{\sigma}_a = \pi r_0^2 (c/v) Z_{\text{eff}} \quad \text{and} \quad \Gamma^{(a)} = \pi r_0^2 c \rho_{\text{ep}}, \quad (3)$$

where the first equation defines  $Z_{\text{eff}}$  [14] (see also [15]),  $r_0$  is the classical electron radius, and  $\rho_{\text{ep}}$  is the electron–positron contact density in the (quasi) bound state ( $\rho_{\text{ep}} \approx 0.1\kappa$ , where  $\kappa = \sqrt{2|\varepsilon_0|}$  [7]), we have

$$Z_{\text{eff}} = \frac{2\pi^2 \rho_{\text{ep}}}{k} \frac{\Gamma^{(e)}(\varepsilon)}{\Gamma(\varepsilon)} \rho(\varepsilon + |\varepsilon_0|). \quad (4)$$

For a simple molecule at low energy,  $\Gamma^{(e)}$  is likely to be greater than  $\Gamma^{(a)} \sim 1$   $\mu\text{eV}$ , so  $\Gamma \approx \Gamma^{(e)}$ , and  $Z_{\text{eff}}$  is proportional to the vibrational spectrum density.

## 4. Vibrational spectrum densities

Assuming  $\Gamma^{(e)}/\Gamma \approx 1$ , we can use Eq. (4) to extract the density  $\rho$  required to reproduce  $Z_{\text{eff}}$  observed at room temperature (Table 1), and compare it with the calculations. To calculate the vibrational spectrum density of  $C_nH_{2n+2}$  we use harmonic approximation,  $E_v = \sum_k n_k \omega_k$ , where the sum is over the modes,  $n_k$  are non-negative integers, and  $\omega_k$  are the mode frequencies from NIST ( $n \leq 4$ ) or calculated using the Q-Chem package [16]. Harmonic vibrational frequencies were calculated using the EDF1 density functional [17], the SG-1 quadrature grid [18] and the 6–31G\* basis set. The resulting frequencies were scaled by 0.97 to account for the neglect of anharmonicity and the incomplete treatment of electron correlation.

The spectrum density  $\rho(E)$  is defined as the number of energy levels per unit energy interval. Its reciprocal is the mean spacing between the vibrational levels at a given energy. A numerical calculation of the density is performed by binning the vibrational excitation energy (we use 1  $\text{cm}^{-1}$  bins in the range 0–4000  $\text{cm}^{-1}$ ), and determining the number of energies  $E_v$  in each bin. For thermal (room-temperature) positrons the density must be averaged over the Maxwellian distribution,

$$\bar{\rho}(|\varepsilon_0|) = \int_0^\infty \rho(|\varepsilon_0| + k^2/2) \frac{e^{-k^2/2k_B T}}{(2\pi k_B T)^{3/2}} 4\pi k^2 dk, \quad (5)$$

where  $T$  is the temperature and  $k_B$  is the Boltzmann constant. The results are shown in Fig. 1.

To test the possible effect of symmetry, we also calculate the densities of the fully symmetric ( $A_1$  or  $A_g$ ) vibrations, see Fig. 1 (right panel). To this end the alkane molecules were assumed to have either  $C_{2v}$  (odd  $n$ ) or  $C_{2h}$  (even  $n$ ) symmetry groups.<sup>1</sup> These have four one-dimensional irreducible representations,  $A_{1,2}$  and  $B_{1,2}$ , or  $A_{g,u}$  and  $B_{g,u}$ . As a result, approximately 25% of the vibrational states are of  $A_1$  ( $A_g$ ) symmetry, and the corresponding

<sup>1</sup> Of course, assuming such “ideal” structures is an approximation. In reality, owing to the low vibrational frequencies of the carbon backbone, the gaseous alkane molecules are twisted into a variety of shapes.

Table 1

Vibrational spectrum densities derived from experimental  $Z_{\text{eff}}$  and binding energies

Molecule	$Z_{\text{eff}}^{\text{a}}$	$ \varepsilon_0 ^{\text{b}}$ (meV)	$\rho_{\text{ep}}^{\text{c}}$ (a.u.)	$\rho^{\text{d}}$ (meV $^{-1}$ )
C <sub>3</sub> H <sub>8</sub>	3500	12	$3.0 \times 10^{-3}$	0.11
C <sub>4</sub> H <sub>10</sub>	11,300	35	$5.3 \times 10^{-3}$	0.20
C <sub>5</sub> H <sub>12</sub>	37,800	60	$7.0 \times 10^{-3}$	0.50
C <sub>6</sub> H <sub>14</sub>	120,000	80	$8.1 \times 10^{-3}$	1.34
C <sub>7</sub> H <sub>16</sub>	242,000	105	$9.2 \times 10^{-3}$	2.45
C <sub>8</sub> H <sub>18</sub>	585,000	120	$9.9 \times 10^{-3}$	5.51
C <sub>9</sub> H <sub>20</sub>	643,000	140	$1.06 \times 10^{-2}$	5.66

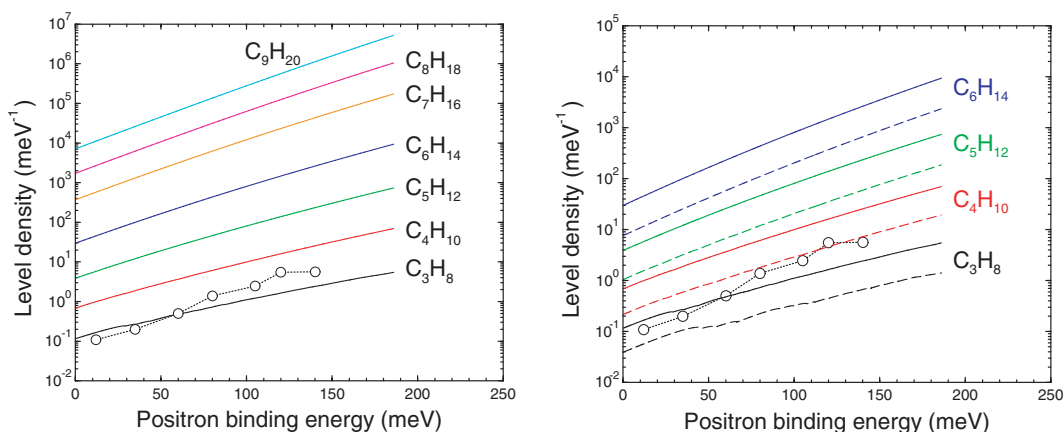
<sup>a</sup> Measured for room- $T$  positrons [5] ( $k \sim 0.05$  a.u.).<sup>b</sup> Estimated from the shifts of C–H peaks [8,9].<sup>c</sup> Estimated using  $\rho_{\text{ep}} \sim 0.1 \sqrt{2|\varepsilon_0|}$  [7].<sup>d</sup> Vibrational density from Eq. (4), assuming  $\Gamma^{(\text{e})}/\Gamma = 1$ .

Fig. 1. Thermally-averaged vibrational spectrum densities for alkanes as functions of the positron binding energy. Solid curves are calculations which included vibrational states of all symmetries. Dashed curves (right panel) are the densities of fully symmetric vibrations ( $A_1$  or  $A_g$ ). Open circles show values inferred for C<sub>3</sub>H<sub>8</sub> to C<sub>9</sub>H<sub>20</sub> from room temperature  $Z_{\text{eff}}$  (Table 1).

densities in Fig. 1 are about a factor of 4 lower than the total ones.

We see that the calculated densities can account for huge room-temperature values of  $Z_{\text{eff}}$ . However, they increase much more rapidly with the size of the molecule. Thus, either not all of the vibrations take part, or  $\Gamma^{(\text{e})} \ll \Gamma$ , or both. On the other hand, it is clear that complex multimode vibrations must be involved. If one assumed that positron capture was accompanied only by simple excitations of the fundamentals, the density of the corresponding resonances would be proportional to the number of modes. Hence, the resulting  $Z_{\text{eff}}$  would grow linearly with the size of the molecule,

which contradicts the experimental data. The understanding of the importance of multimode vibrational resonances must be reconciled with the recent experimental findings which show that peaks in the energy dependence of  $Z_{\text{eff}}$  correlate with the positions of molecular vibrational modes [8,9].

## 5. Vibrational doorways

A possible explanation of the prominence of single-mode vibrations in the process of positron capture into multimode excitation resonances, can

be formulated using the notion of “doorway” states. This term originates from nuclear physics, where it means ‘a metastable state formed in the initial state of the reaction’, which ‘may decay partly into the open channels (direct reactions), and partly through the coupling to the internal degrees of freedom’ [19].

In application to the low-energy positron–molecule collisions problem, we suggest that positron capture proceeds in two steps. The positron first forms a bound state with the molecule, and the excess energy is transferred into an excitation of a fundamental. This simple *doorway* state of the positron–molecule complex is embedded in the dense spectrum of multimode vibrations. Due to vibrational state mixing, the doorway state then decays or “spreads” into the multimode vibrational states. Such decay takes place on the time scale  $\tau \sim 1/\Gamma_{\text{spr}}$ , where  $\Gamma_{\text{spr}}$  is known as the spreading width.

To link the multimode VFR and doorway state resonance pictures together, consider the positron capture (or re-emission) width,

$$\Gamma_v^{(e)} = 2\pi |\langle \Psi_v | V | 0, \varepsilon \rangle|^2, \quad (6)$$

where  $|0, \varepsilon\rangle$  describes positron incident on the ground-state molecule, and  $V$  is coupling between the incident positron and VFR  $|\Psi_v\rangle$ . The latter is a linear combination,

$$|\Psi_v\rangle = \sum_i C_i^{(v)} |\Phi_i\rangle, \quad (7)$$

of *harmonic* vibrational basis states  $|\Phi_i\rangle$ .

Let us assume that of all  $|\Phi_i\rangle$  states only those which describe ‘bound positron + single-mode excitation’,  $|n, \varepsilon_0\rangle$ , contribute. The coefficients  $C_i^{(v)}$  describe mixing of this state with the multimode eigenstates  $v$  (i.e. its “spreading”), and can be approximated by a Breit–Wigner shape (subject to normalisation  $\sum_i |C_i^{(v)}|^2 = 1$ ):

$$|C_i^{(v)}|^2 \propto \frac{\Gamma_{\text{spr}}^2/4}{(E_v - E_i)^2 + \Gamma_{\text{spr}}^2/4}. \quad (8)$$

Using Eqs. (4), (6), (7) and (8) (see [20] for the details of a similar derivation), one obtains  $Z_{\text{eff}}$  averaged over the energy on the scale of closely spaced VFR, as a sum over the fundamentals:

$$Z_{\text{eff}} = \frac{2\pi^2 \rho_{\text{ep}}}{k} \frac{\Gamma_{\text{spr}}}{2\pi \Gamma(\varepsilon)} \sum_n \frac{\Gamma_n^{(e)}}{(\varepsilon - \omega_n - \varepsilon_0)^2 + \frac{1}{4} \Gamma_{\text{spr}}^2}, \quad (9)$$

where  $\Gamma_n^{(e)} = 2\pi |\langle n, \varepsilon_0 | V | 0, \varepsilon \rangle|^2$  is the capture width of the doorway state  $n$ .

## 6. Energy dependence of $Z_{\text{eff}}$

If  $\Gamma(\varepsilon)$  is a smooth function and  $\Gamma_n^{(e)} \approx \text{const}$ , the energy dependence of  $Z_{\text{eff}}$ , Eq. (9), is determined by the spectrum of fundamentals:

$$S(\varepsilon) = \frac{\Gamma_{\text{spr}}}{2\pi} \sum_n \frac{1}{(\varepsilon - \omega_n - \varepsilon_0)^2 + \frac{1}{4} \Gamma_{\text{spr}}^2}, \quad (10)$$

so that

$$Z_{\text{eff}} \approx \underbrace{\frac{2\pi^2 \rho_{\text{ep}}}{k}}_{\sim 1 \text{ a.u.}} \times \underbrace{\frac{\Gamma_n^{(e)}}{\Gamma(\varepsilon)}}_{\text{dimensionless}} \times S(\varepsilon) \equiv AS(\varepsilon). \quad (11)$$

For non-monoenergetic positrons,  $S(\varepsilon)$  must be folded with the energy-resolution function. Let us approximate the positron energy distribution by a Lorentzian profile with a certain width (experimentally, its full width at half maximum (FWHM) is about 25 meV). Then  $S(\varepsilon)$  retains its form (10), but the width must be replaced by the *sum* of  $\Gamma_{\text{spr}}$  and FWHM of the beam. Assuming that  $\Gamma_{\text{spr}}$  is the smaller of the two contributions, we can use Eq. (10) and formally put  $\Gamma_{\text{spr}} = 25$  meV in it.

To compare the energy dependence predicted by the doorway-state model, Eq. (11), with experiment, we use  $A$  and  $\varepsilon_0$  as free parameters, aiming to fit the data in the vicinity of the prominent (C–H stretch) peaks. The results are shown in Fig. 2. The systematic downshift of the C–H peak is the strongest experimental evidence so far for positron–molecule binding [9]. Values of  $\varepsilon_0$  give energies of the positron–molecule bound states, while the rapid growth of  $A$  should be attributed to the decrease of the total width of positron–molecule VFR with the increasing complexity of the molecule.

Another remarkable feature of the data in Fig. 2 is an overall similarity between the experimental  $Z_{\text{eff}}$  and that from Eq. (11). This means that lower-lying modes also act as doorways for the positron

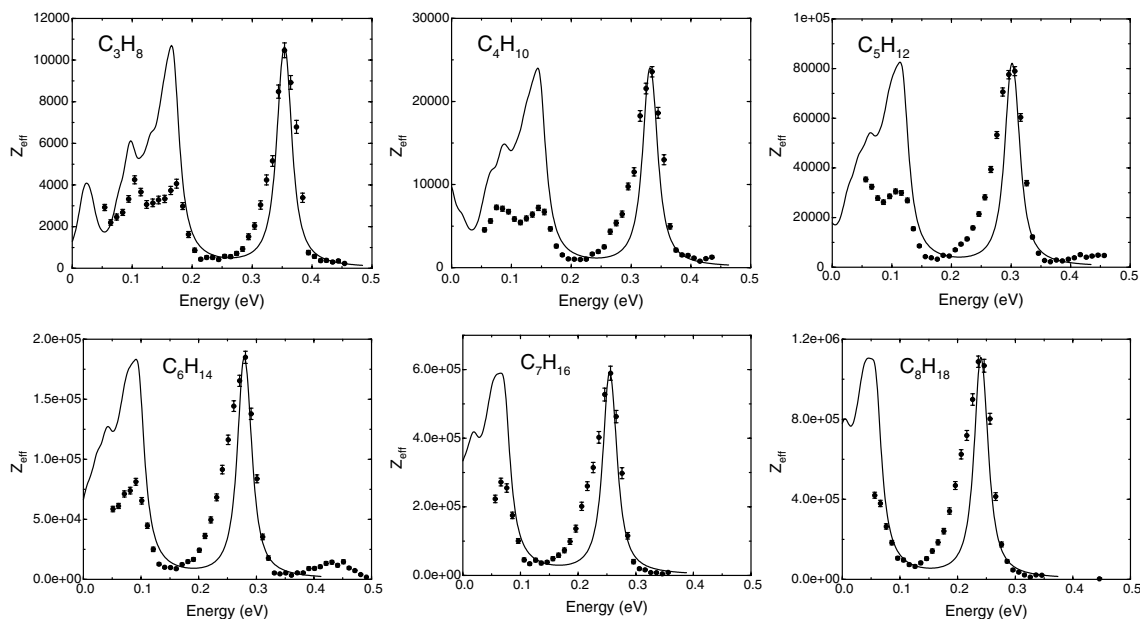


Fig. 2. Two-parameter fits  $AS(\varepsilon)$  (solid curves) of the C–H stretch maxima of experimental  $Z_{\text{eff}}$  [9] (solid circles).  $\text{C}_3\text{H}_8$ :  $A = 58$ ,  $\varepsilon_0 = -0.012$  eV;  $\text{C}_4\text{H}_{10}$ :  $A = 105$ ,  $\varepsilon_0 = -0.033$  eV;  $\text{C}_5\text{H}_{12}$ :  $A = 300$ ,  $\varepsilon_0 = -0.062$  eV;  $\text{C}_6\text{H}_{14}$ :  $A = 575$ ,  $\varepsilon_0 = -0.084$  eV;  $\text{C}_7\text{H}_{16}$ :  $A = 1600$ ,  $\varepsilon_0 = -0.108$  eV;  $\text{C}_8\text{H}_{18}$ :  $A = 2650$ ,  $\varepsilon_0 = -0.122$  eV.  $\text{C}_9\text{H}_{20}$  is similar, with  $A = 5700$  and  $\varepsilon_0 = -0.164$  eV.

capture and annihilation. A somewhat poorer description of the height of the low-energy peaks and the asymmetry of the C–H stretch peak by the model is most likely a consequence of our use of a single  $\Gamma_n^{(c)}$  value and constant  $A$  in Eq. (11). The present comparison also lends support to an observation that a larger difference between thermal  $Z_{\text{eff}}$  and that at the C–H peak in heavier alkanes ( $\text{C}_9\text{H}_{20}$  and  $\text{C}_{12}\text{H}_{26}$ ) is related to the shift of the minimum into the range of thermal energies [9]. Within the doorway picture, this results from a lack of single-mode doorways in the thermal energy range for such molecules.

## 7. Conclusions

A mechanism of annihilation via positron capture into vibrational Feshbach resonances has been considered. We have shown that high vibrational spectrum densities in alkanes can in principle explain thermal  $Z_{\text{eff}}$ . However, their increase with the molecular size (Fig. 1) indicates that for molecules larger than butane not all modes are

involved, or that the capture width is becoming smaller than the annihilation width.

Examination of the energy dependence of  $Z_{\text{eff}}$  and its comparison with a simple sum over the normal modes (11), Fig. 2, suggest that positron capture is mediated by the fundamental vibrational doorway states. In this picture large  $Z_{\text{eff}}$  values are caused by small total widths  $\Gamma$  of the VFR, which is a consequence of the dense spectrum of VFR's (i.e.  $\Gamma_n^{(c)}$  are shared by many resonances). The drop of  $Z_{\text{eff}}$  at higher positron energies can then be associated with the onset of vibrational excitation quenching of  $Z_{\text{eff}}$ , which causes a rapid increase of the total width of VFR and reduces the probability of annihilation. Vibrational excitation quenching may also be responsible for the suppression of the C–H stretch peak upon fluorination [9].

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