

# Dependence of resonant positron-molecule annihilation on molecular temperature

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## Abstract

Measurements of positron-on-molecule annihilation as a function of positron energy have established that positrons can bind to hydrocarbon molecules via vibrational Feshbach resonances. The magnitudes of these resonances, which grow rapidly with increasing molecular size, are still not well understood. In this paper, the role of molecular temperature is investigated using a specially designed temperature-regulated annihilation cell. Only relatively small changes in annihilation rate are observed when the molecular temperature is varied by a factor of two, from 300 K down to approximately half that value for the alkane molecules pentane and heptane. These results place important constraints on theories of the annihilation rates and positron-molecule binding energies.

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## 1. Introduction

Studies using trap-based positron beams with narrow energy spreads have clarified greatly many of the possible interactions of positrons with isolated atoms and molecules [1–3]. It is now clear that positrons with appropriate incident energies  $\epsilon$  can form temporary bound states with molecules via vibrational Feshbach resonances (VFR). This results in substantially enhanced annihilation rates at a fixed binding energy,  $\epsilon_b$ , below the fundamental vibrational modes of the molecule.

Annihilation rates are typically expressed in terms of a normalized dimensionless parameter,  $Z_{\text{eff}}$ , given by

$$Z_{\text{eff}} = \frac{\Gamma}{\pi r_0^2 c n_m}, \quad (1)$$

where  $\Gamma$ ,  $r_0$ ,  $c$  and  $n_m$  are the measured annihilation rate, the classical electron radius, the speed of light, and the

density of the molecular gas, respectively. Expressed in this way,  $Z_{\text{eff}}$  is the annihilation rate for a given density of molecules normalized by the rate of annihilation for an identical density of free electrons. For a model in which the positron and the molecular electrons are completely uncorrelated, one would expect  $Z_{\text{eff}} \sim Z$ , where  $Z$  is the number of electrons on the molecule. In contrast, as shown in Fig. 1,  $Z_{\text{eff}}$  can be orders of magnitude larger due to VFR-mediated annihilation.

Both  $Z_{\text{eff}}$  and the positron-molecule binding energy,  $\epsilon_b$ , vary greatly with molecular species but, in general, grow with molecular size. For example, in alkanes (molecular chains of the form  $C_nH_{2n+2}$ ), resonant  $Z_{\text{eff}}$  grows exponentially with the number of carbon atoms. At the same time, it is found experimentally that  $\epsilon_b$  grows linearly with the number of carbon atoms, such that  $Z_{\text{eff}} \propto (2n+2)e^{(\epsilon_b/\epsilon_0)}$  where  $\epsilon_0 \approx 26$  meV [4,5]. We note, however, that this scaling fails for other molecules such as aromatics. Also, recent experimental evidence indicates that resonant  $Z_{\text{eff}}$  depends only weakly on  $\epsilon_b$  via a scale factor  $g = \sqrt{\epsilon_b/\epsilon}$  [6,7]. Thus the origin of the large enhancement in  $Z_{\text{eff}}$  in large molecules remains to be explained.

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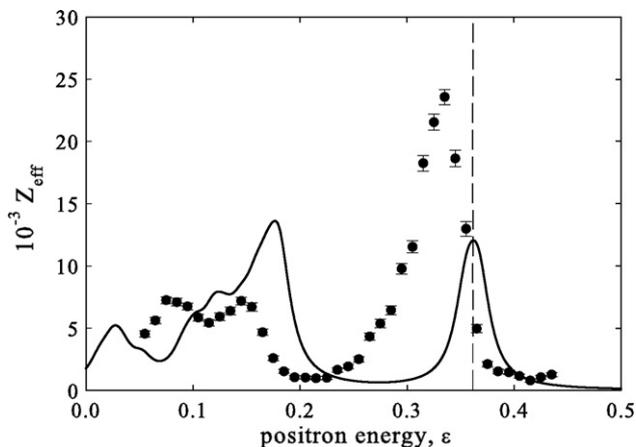


Fig. 1.  $Z_{\text{eff}}$  spectrum (●) for butane ( $\text{C}_4\text{H}_{10}$ ) as a function of positron energy,  $\epsilon$ , from [4]. The solid curve (–) shows the fundamental vibrational modes of butane, convolved with a 25 meV Lorentzian function and scaled arbitrarily. The vertical dashed line indicates the position of the C–H stretch mode. Note that the  $Z_{\text{eff}}$  peaks are shifted by an amount  $\epsilon_b \sim 35$  meV below the vibrational mode peaks.

According to a successful theory of VFR-enhanced annihilation [8,9], for positrons with incident energy,  $\epsilon$ , the magnitudes of the  $Z_{\text{eff}}$  resonances are proportional to the density of accessible molecular vibrational states,  $\rho(\epsilon + \epsilon_b)$ ; the positron capture (and emission) rate,  $\Gamma^{(e)}$ ; and the annihilation rate in a particular state,  $\Gamma^{(a)}$ , normalized by the rate of all possible post-capture processes, namely,

$$Z_{\text{eff}}(\epsilon) \propto \rho(\epsilon + \epsilon_b) \frac{\Gamma^{(e)}\Gamma^{(a)}}{\Gamma^{(e)} + \Gamma^{(a)} + \Gamma^{(o)}}, \quad (2)$$

where  $\Gamma^{(o)}$  is the total rate due to inelastic escape channels. Thus, the normalized rate,  $Z_{\text{eff}}$ , is reduced if the bound positron is allowed to escape via these additional inelastic channels. That said, as the binding energy increases, fewer inelastic channels have sufficient energy to unbind the positron before annihilation.

In principle, thermally excited modes can also stimulate positron detachment, contributing to the overall inelastic width described above. In the simplest picture, the probability that a given degree of freedom has sufficient energy to unbind the positron decreases exponentially with binding energy at a rate proportional to the Boltzmann factor,  $\exp(-\epsilon_b/k_B T)$ , where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. As  $T$  decreases, so does the probability of thermal detachment, resulting in an increase in  $Z_{\text{eff}}$  determined by the binding energy and the mode density.

In this paper, we seek to determine the relative influence of thermally excited modes on positron binding and  $Z_{\text{eff}}$ . One further motivation is to explore the close correspondence between the empirical scaling in alkanes,  $Z_{\text{eff}} \propto (2n + 2)e^{\epsilon_b/\epsilon_0}$  and the reciprocal of the Boltzmann factor. If this relationship were valid, resonant values of  $Z_{\text{eff}}$  in alkanes would be entirely determined by the molec-

ular temperature, and so lowering the temperature of the target gas should result in a dramatic increase in  $Z_{\text{eff}}$ .

To test these ideas, we performed experiments on two alkane molecules, pentane ( $\text{C}_5\text{H}_{12}$ ) and heptane ( $\text{C}_7\text{H}_{16}$ ), using a specially constructed cold cell designed to measure the magnitude and energy spectrum of  $Z_{\text{eff}}$  for test-gas temperatures between 300 K and approximately half that value. In contrast to the possibilities described above, the data show a relatively modest temperature dependence over this range. These results place important constraints on theoretical models of VFR-enhanced annihilation.

## 2. Experiment

The experimental apparatus and procedures for measuring  $Z_{\text{eff}}$  as a function of positron impact energy at 300 K are described in detail elsewhere [2,4,10]. In brief, positrons from a 50 mCi  $^{22}\text{Na}$  source are moderated by a solid neon moderator and guided by a magnetic field into a three-stage, Penning–Malmberg, buffer-gas accumulator. The positrons are trapped via inelastic collisions with  $\text{N}_2$  molecules and cooled to room temperature via collisions using a gas mixture of  $\text{N}_2$  and  $\text{CF}_4$ . Cold, energy-tunable pulses of positrons are then guided magnetically into a cell filled with the test-gas. The electrical potential on a cylindrical electrode in the cell sets the positron energy in the interaction region.

The cell is baffled at both ends and surrounded outside the vacuum chamber with lead to shield the detector from spurious annihilation gamma-rays coming from outside the cell. Single, 511 keV gamma rays from the two-gamma annihilation events are detected using a CsI detector. Typically, the baffle immediately after the gas cell, referred to as the back baffle, has a positive bias to reflect the incident positrons, so that the positron pulses may pass through the gas cell multiple times within a predetermined time window. Absolute values of  $Z_{\text{eff}}$  are determined using measurements of the positron pulse strength, positron energy, path length and the test-gas pressure.

The cold cell apparatus, which is shown schematically in Fig. 2, functions in a manner similar to the 300 K cell used

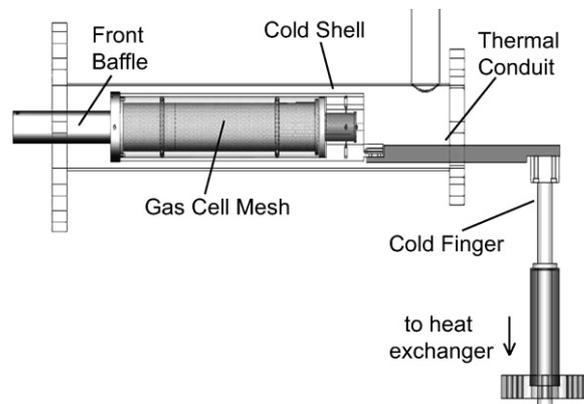


Fig. 2. Schematic diagram of the cold cell apparatus (not to scale). For reference, the length of the gas cell mesh is 27 cm.

in previous measurements, with the exception that it has been redesigned to allow for controlled cooling and temperature measurements. The previous gas cell and back electrode were replaced by electrically isolated, gold-plated copper meshes inside a copper “cold shell”. The meshes are used to set the electrical potential inside the gas cell, while the conduction-cooled, baffled shell contains and cools the test-gas. The cold shell is designed to freeze out large impurity molecules in the vacuum system and thus keep the meshes relatively clean. The cold shell rests on stainless-steel standoffs to thermally isolate it from the vacuum chamber and is connected by a copper bar to a thermally insulated vacuum feed through. The feed through is connected to an open-ended heat exchanger outside the vacuum chamber that operates on pulses of liquid N<sub>2</sub> from a supply dewar and exhausts into the atmosphere.

The test-gas cell can be cooled to ~100 K with a ~10–15 K variation from one end of the cell to the other. The temperature is measured by a diode on each side of the cold shell and a platinum resistive temperature device (RTD) on the outside of the feed through. The RTD and a proportional-integral-differential controller are used to switch on and off the flow of liquid N<sub>2</sub> to maintain a constant (i.e. set-point) temperature.

One of the most important constraints in this experiment is the operating range of test-gas temperatures. It is limited by the temperature of liquid N<sub>2</sub> at atmospheric pressure (i.e. 77 K) and the conduction of the copper bar connecting the heat exchanger to the gas cell. Moreover, it is also limited by the vapor pressure of the test-gas, which decreases with temperature and must be kept higher than the operating pressure in the cell to prevent condensation inside or outside the gas cell. The operating pressure itself must be maintained high enough for good signal to noise, but low enough to keep total scattering low (i.e. below about 15%). Since the vapor pressures and condensation temperatures of alkanes decrease with increasing molecular size, so does the minimum operating temperature. This places a significant constraint on studies of larger alkane molecules.

The pressure of the test-gas is measured both by a manometer, connected via a tube to one end of the gas cell and by an ion gauge near the gas inlet outside the back baffle. The manometer provides an absolute measure of the gas pressure after applying an equal-flux temperature correction, namely

$$P_m = P_c \sqrt{T_m/T_c}, \quad (3)$$

where the subscripts m and c refer to the manometer and gas cell, respectively. While the ion gauge has a gas-dependant correction factor, it has the advantage that it can measure the low operating pressures needed to study alkanes with large  $Z_{\text{eff}}$ . This correction factor is determined empirically by comparing manometer and ion gauge readings at several pressures below the vapor pressure of the test-gas.

Above the test-gas vapor pressure, liquid starts to condense in the cell and the thermal conduit from the heat

exchanger. In this case, the pressure read by the ion gauge in the warm region grows rapidly, while the manometer pressure (which measures the pressure inside the cell) remains relatively constant. In this case, the cold cell is acting as a cryopump. Observation of this phenomenon provides evidence that the test gas is, in fact, making a sufficient number of inelastic collisions to cool to the cell temperature. In addition, at the cold temperatures for which data are presented, the test molecules, pentane and heptane, have an appreciable probability (e.g.  $\geq 50\%$ ) of sticking on the cold electrodes upon each collision [11–13]. It is estimated that a large molecule entering the cold cell will make ~50 collisions with the cell walls, over the course of ~5 ms, before exiting the cell. Thus, equilibration of the nuclear degrees of freedom with the electrode temperature is a good assumption.

### 3. Results

The cold cell was used to measure  $Z_{\text{eff}}$  as a function of temperature for two alkane molecules, pentane (C<sub>5</sub>H<sub>12</sub>) and heptane (C<sub>7</sub>H<sub>16</sub>). In each case, energy resolved  $Z_{\text{eff}}$  spectra were measured at both room temperature and at a cold temperature below 200 K (adjusted for each test species so that the equilibrium vapor pressure was a safe margin above the set test-gas pressure in the cell). Pentane was measured at 15.5  $\mu\text{torr}$  and 153 K and heptane at 1.34  $\mu\text{torr}$  and 195 K. For reference, the “peak desorption temperature” for these molecules, which is the temperature at which the surface sticking coefficient goes to zero, is 168 K and 211 K, respectively, on a Cu(111) surface [13].

The resulting energy spectra for  $Z_{\text{eff}}$  are shown in Figs. 3 and 4, where they are compared with spectra measured at test-gas temperatures of 300 K. For both molecules, there was relatively little change in the magnitude or shape of  $Z_{\text{eff}}$  in response to the significant change in temperature. Most of the change in  $Z_{\text{eff}}$  that did occur was observed at lower positron impact energies. Specifically, at low-temperature and smaller at values of positron energy,  $Z_{\text{eff}}$  increased by ~30% in pentane and ~50% in heptane.

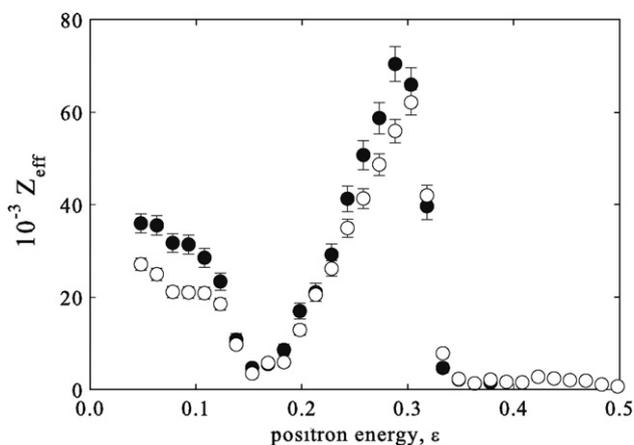


Fig. 3. Energy-resolved  $Z_{\text{eff}}$  for pentane (C<sub>5</sub>H<sub>12</sub>) at 300 K (○) and 153 K (●).

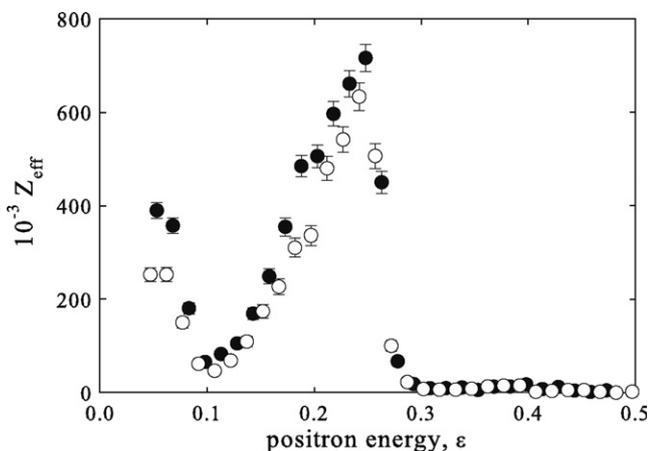


Fig. 4. Energy-resolved  $Z_{\text{eff}}$  for heptane ( $\text{C}_7\text{H}_{16}$ ) at 300 K ( $\circ$ ) and 195 K ( $\bullet$ ).

We note that, in Figs. 3 and 4, there is a slight broadening of the  $Z_{\text{eff}}$  peaks compared with previous measurements (e.g., Fig. 1 and [4,10]). Since this occurs consistently for both the room- and low-temperature measurements in all of the targets studied, it is likely due to a broader positron energy distribution within the gas cell. It could be caused either by positron scattering or by variations in electrical potential due to the metal mesh inside the gas cell. Also note that the positions of the  $Z_{\text{eff}}$  peaks are unaltered when the temperature is changed, indicating that there is little change in the binding or vibrational mode energies. The preciseness of the match between the high- and low-temperature measurements, both in magnitude and energy spectrum, indicates that the relative systematic errors between high- and low-temperature measurements are small. This is non-trivial because a different calibration factor for density and particle flux must be used at each temperature.

The spectra of  $Z_{\text{eff}}$  for propane ( $\text{C}_3\text{H}_8$ ) and butane ( $\text{C}_4\text{H}_{10}$ ) were also measured at temperatures of 133 K and at 151 K, respectively. Unfortunately, at these temperatures, the probability that these molecules stick to copper is infinitesimal [11–13]. For this reason, it is more difficult to guarantee that these molecules are completely thermalized in the cold cell. That said, propane and butane showed no change in  $Z_{\text{eff}}$  with temperature within the measurement errors, which were similar to those shown in Figs. 3 and 4 for pentane and heptane. This is also non-trivial considering that temperature-dependent calibration factors were used to derive the absolute values of  $Z_{\text{eff}}$ . Thus, although it was not possible for us to corroborate, these molecules may well have thermalized by a combination of collisions with the irregular copper-oxide layer on the gas cell walls and adsorption on the colder thermal conduit before entering the gas cell.

#### 4. Discussion and summary

Measurements are presented here for the energy spectra of  $Z_{\text{eff}}$  for pentane and heptane over approximately a factor of 2 and 1.5 reduction in temperature, respectively. The

spectral shapes remain the same for both molecules, while the magnitudes of  $Z_{\text{eff}}$  change only in the regions of the fundamental vibrational modes; they increase at low-temperatures by up to 50% in the lower-frequency parts of the spectrum and <10% near the C–H stretch peak.<sup>1</sup> This lack of a strong temperature-dependence of  $Z_{\text{eff}}$  eliminates the postulated Boltzmann-factor-like scaling of  $Z_{\text{eff}}$  with binding. If that scaling were correct, the C–H stretch peak in pentane should have grown by a factor of ten as the temperature was lowered by the amount indicated.

There are no accurate theoretical predictions of the magnitudes of  $Z_{\text{eff}}$  resonances (or even the relative magnitudes of resonances) in larger molecules.<sup>2</sup> This, in turn, complicates the task of unraveling the origin of the relatively weak temperature dependence reported here. To lowest order, if the rate of elastic positron escape is much larger than the rate of thermally assisted escape from the molecule, the temperature-dependence should be negligible. One could argue that this is the case for the C–H stretch resonance but not so much for the lower energy resonances (e.g., those due to the C–H bend and C–C stretch modes).

The temperature-independence of the binding energy apparently rules out one model of positron binding. In particular, it was suggested that a change in the bond geometry might be required for a positron to bind to a molecule (and thus be required for VFR-mediated annihilation) [14,15]. For example, it was predicted that a change in the C–C–H bond angle of  $19^\circ$  would be required for binding to acetylene ( $\text{C}_n\text{H}_{2n+2}$ ) [14]. As a result, binding could occur only if the molecule were in a highly excited vibrational state. One way to control the level of vibrational excitation is to change the temperature (i.e. “hot” molecules would be expected to have deeper binding than “cold” molecules). By extension, hot molecules would also be more likely to have VFR annihilation peaks (or have larger peaks). The cold cell data presented here show no evidence of this effect, namely the binding energy is constant over a factor of approximately two change in molecular temperature.

The results described here place important constraints on theories of positron-molecule annihilation. The positron-molecule binding energy does not change with molecular temperature. Explicit thermal detachment processes are shown to be relatively weak. This conclusion that inelastic channels seem to be generally weak or inactive in large molecules is consistent with a recent study of the scaling of  $Z_{\text{eff}}$  with positron binding energy [7].

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<sup>1</sup> For comparison, the systematic error in the magnitude of  $Z_{\text{eff}}$  in this experiment is estimated to be  $\sim 20\%$ .

<sup>2</sup> In such molecules, it is believed that the initial resonant excitation (e.g., the C–H stretch) is coupled to other (“dark-state”) resonances, which results in increased magnitudes of resonant  $Z_{\text{eff}}$  [9].

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