

Mechanisms of positron annihilation on molecules

G. F. Gribakin*

School of Physics, University of New South Wales, Sydney 2052, Australia

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The aim of this work is to identify the mechanisms responsible for very large rates and other peculiarities observed in low-energy positron annihilation on molecules. The two mechanisms considered are the following: (i) Direct annihilation of the incoming positron with one of the molecular electrons. This mechanism dominates for atoms and small molecules. I show that its contribution to the annihilation rate can be related to the positron elastic scattering cross section. This mechanism is characterized by a strong energy dependence of Z_{eff} at small positron energies and high Z_{eff} values (up to 10^3) for room-temperature positrons, if a low-lying virtual level or a weakly bound state exists for the positron. (ii) Resonant annihilation, which takes place when the positron undergoes resonant capture into a vibrationally excited quasibound state of the positron-molecule complex. This mechanism dominates for larger molecules capable of forming bound states with the positron. For this mechanism Z_{eff} averaged over some energy interval, e.g., due to thermal positron energy distribution, is proportional to the level density of the positron-molecule complex, which is basically determined by the spectrum of molecular vibrational states populated in the positron capture. The resonant mechanism can produce very large annihilation rates corresponding to $Z_{\text{eff}} \sim 10^8$. It is highly sensitive to molecular structure, and shows a characteristic $\varepsilon^{-1/2}$ behavior of Z_{eff} at small positron energies ε . The theory is used to analyze calculated and measured Z_{eff} for a number of atoms and molecules.

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I. INTRODUCTION

The aim of this work is to develop a framework for the description of low-energy positron annihilation on molecules, and to analyze its two main mechanisms: direct and resonant annihilation. There are a number of remarkable phenomena associated with this process: very large annihilation rates [1–3], high sensitivity of the rates to small changes in the molecular structure [4], large ionization-fragmentation cross sections for organic molecules at sub-Ps-threshold positron energies [5], and rapid increase of the fragmentation and annihilation rates toward small positron energies [6,7]. In spite of decades of study, there is no consistent physical picture or even general understanding of these processes, and there have been very few calculations [8], which leaves too much room for speculation [9]. My main objectives are to consider real mechanisms of positron annihilation on molecules, describe their characteristic features, make estimates of the corresponding annihilation rates, and formulate the terms in which positron-molecule annihilation should be described and analyzed. In Ref. [7], Iwata *et al.* described new experiments to study positron annihilation on molecules. Some of these experiments test specific features of the annihilation processes described in the present paper. Though some aspects of the experimental work are discussed here, further details and comparison with theory and various models of positron annihilation can be found in Ref. [7].

The annihilation rate λ for positrons in a molecular or atomic gas is usually expressed in terms of a dimensionless parameter Z_{eff} ,

$$\lambda = \pi r_0^2 c Z_{\text{eff}} n, \quad (1)$$

where r_0 is the classical radius of the electron, $\pi r_0^2 c$ is the nonrelativistic spin-averaged rate of electron-positron annihilation into two γ quanta, and n is the number density of molecules [10]. Equation (1) implies that Z_{eff} is the effective number of target electrons contributing to the annihilation process. In terms of the annihilation cross section σ_a the rate is $\lambda = \sigma_a n v$, so, by comparison with Eq. (1), we have

$$\sigma_a = \pi r_0^2 c Z_{\text{eff}} / v, \quad (2)$$

where v is the positron velocity. Accordingly, the spin-averaged cross section of annihilation of a nonrelativistic positron on a single electron corresponds to $Z_{\text{eff}} = 1$; see, e.g. Ref. [11]. If the annihilation occurs during binary positron-molecule collisions, as in the experiments of the San Diego group [3,4,12], who used a positron trap and worked at low gas densities, the parameter Z_{eff} is independent of the density. It characterizes the annihilation of a positron on a single molecule.

One could expect that Z_{eff} is comparable to the number of electrons Z in an atom or molecule. Moreover, low-energy positrons do not penetrate deep into the atom, and most probably annihilate with the valence electrons only. However, even for hydrogen $Z_{\text{eff}} = 8$ at low energies [13]. This is a manifestation of correlation effects. The most important of these is polarization of the atom by the positron and, as a result, an attractive $-\alpha e^2/2r^4$ positron-atom potential, α being the atomic dipole polarizability. An additional short-range contribution to the positron-atom attraction comes from virtual Ps formation, i.e., hopping, or rather, tunneling of an electron between the atomic ion and the positron. The electron density on the positron is also enhanced due to the

*Present address: Department of Applied Mathematics and Theoretical Physics, The Queen's University of Belfast, Belfast BT7 1NN, UK.

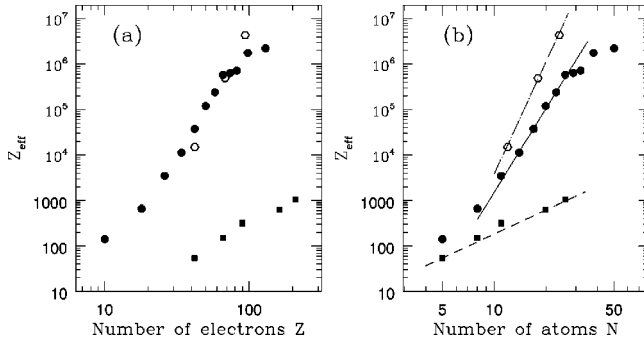


FIG. 1. Annihilation rates Z_{eff} for alkanes, C_nH_{2n+2} (solid circles, $n=1-10, 12,$ and 16), perfluorinated alkanes, C_nF_{2n+2} (solid squares, $n=1-3, 6,$ and 8) and aromatic hydrocarbons, benzene, naphthalene, and anthracene, $C_nH_{n/2+3}$ (open hexagons, $n=6, 10,$ and 14), as functions of the number of electrons in the molecule Z (a), and number of atoms N (b). Data are taken from Ref. [12], Tables B1, 4.3, 4.9 and 4.11 (see also Ref. [4]). Also shown are power-law fits for alkanes, $Z_{\text{eff}} \propto N^{6.1}$ (solid line); perfluorinated alkanes, $Z_{\text{eff}} \propto N^{1.75}$ (dashed line); and aromatic hydrocarbons, $Z_{\text{eff}} \propto N^{8.2}$ (dot-dashed line).

Coulomb attraction between them. These effects make atomic Z_{eff} large, e.g., $Z_{\text{eff}}=401$ for room temperature positrons on Xe [14].

Even compared with this large number, annihilation rates for low-energy (room temperature) positrons on polyatomic molecules are huge. They increase very rapidly with the molecular size, and depend strongly on the chemical composition of the molecules; see Fig. 1. This has been known for quite a while, after early measurements for CCl_4 , $Z_{\text{eff}}=2.2 \times 10^4$ [1]; butane, 1.5×10^4 [2]; and Z_{eff} ranging between 10^4 and 2×10^6 for large alkanes C_nH_{2n+2} , where $n=4-16$ [15] (see also [4]). The largest Z_{eff} values measured so far are 4.3×10^6 for anthracene $C_{14}H_{10}$ [16] and 7.5×10^6 for sebacyc acid dimethyl ester $C_{12}H_{22}O_4$ [15]. Thus, while Z_{eff} 's up to five orders of magnitude greater than Z have been observed, the physical processes responsible for these anomalously large annihilation rates have not really been understood. In other words, if the observed Z_{eff} 's are parametrically large, compared to the number of available electrons, then what are the parameters that determine large annihilation rates for positrons on molecules?

In this work I consider two basic mechanisms of positron-molecule annihilation. The first mechanism is *direct annihilation* of the incoming positron with one of the molecular electrons. The contribution of this mechanism to the annihilation rate is proportional to the number of valence electrons available for annihilation. It can be enhanced by the positron-molecule interaction which distorts the positron wave. In particular, the positron density in the vicinity of the molecule increases greatly if a low-lying virtual state ($\varepsilon_0 > 0$) or a weakly bound level ($\varepsilon_0 < 0$) exists for the s -wave positron. In this case $Z_{\text{eff}}^{(\text{dir})} \propto 1/(\varepsilon + |\varepsilon_0|)$ for small positron energies $\varepsilon \leq |\varepsilon_0|$ [17–19]. This type of enhancement is responsible for large Z_{eff} values observed in heavier noble-gas atoms, where successively lower virtual levels exist for the positron ($Z_{\text{eff}}=33.8, 90.1,$ and 401 for Ar, Kr, and Xe, respectively [4,14]). This understanding is confirmed by the

temperature dependences of the annihilation rates measured for the noble gases in Ref. [20]. Note that for room-temperature positrons, $\varepsilon \sim k_B T$, even for $\varepsilon_0 \rightarrow 0$ the size of the enhancement due to virtual or weakly bound states is limited.

The second mechanism is *resonant annihilation*. By this I mean a two-stage process. The positron is first captured into a Feshbach-type resonance, where positron attachment is accompanied by excitation of some molecular degrees of freedom. Such a process is well known for electrons [21]. The positron in the quasibound state then annihilates with a molecular electron. Enhancement of annihilation due to a single resonance was considered theoretically in Refs. [22,23]. The possibility of forming such resonances by excitation of the vibrational degrees of freedom of molecules was proposed by Surko *et al.* [3] to explain high annihilation rates and their strong dependence on the molecular size observed for alkanes. It was also considered in relation to the problem of fragmentation of molecules by positron annihilation [24]. However, its contribution to the annihilation has never been properly evaluated. To make this mechanism work for low-energy positrons one must assume that positrons can form bound states with large neutral molecules, i.e., the positron affinity of the molecule is positive, $\varepsilon_A > 0$ [3]. Capture is then possible if the energy of the incoming positron is in resonance with the vibrationally excited state of the positron-molecule complex [25]. The density of the vibrational excitation spectrum of this complex can be high, even if the excitation energy supplied by positron binding, $E_v = \varepsilon_A + \varepsilon$, is only a few tenths of an eV (it is reasonable to assume that the presence of the positron does not change the vibrational spectrum of the molecule by too much). For positrons with a thermal Maxwellian energy distribution, the contribution of the resonant annihilation mechanism averaged over a number of resonances $Z_{\text{eff}}^{(\text{res})}$ is observed. The magnitude of $Z_{\text{eff}}^{(\text{res})}$ is determined by three parameters of the positron-molecule resonant states: their annihilation width Γ_a ; the autodetachment width Γ_c , which also determines the probability of positron capture; and the level density $\rho(E_v)$ of the positron-molecule resonant states populated in positron capture. The magnitude of Γ_a for positron-molecule bound states is comparable to the spin-averaged annihilation width of the Ps atom ($\Gamma_a/\hbar \sim 5 \times 10^{-10}$ s). Note that Γ_a does not increase with the size of the molecule, because the increase in the number of electrons is accompanied by a thinning of the positron density in the (quasi)bound positron-molecule state. It turns out (see Sec. II) that for $\Gamma_c \gg \Gamma_a$ the magnitude of $Z_{\text{eff}}^{(\text{res})}$ is simply proportional to $\rho(E_v)$. This density increases rapidly with the size of the molecule, $\rho(E_v) \propto (N_v)^n$, where N_v is the number of vibrational modes, $n \sim \varepsilon_A/\omega$ is the effective number of vibrational quanta excited in positron capture, and ω is a typical molecular vibrational frequency. Thus the resonant annihilation mechanism can explain the rapid increase of Z_{eff} with the size of the molecule shown in Fig. 1. Moreover, my estimates show that for thermal positrons $Z_{\text{eff}}^{(\text{res})}$ up to 10^8 could be observed.

A necessary condition for resonant annihilation to occur is the existence of positron-molecule bound states. Until re-

cently there was almost no positive information about the possibility of positron binding to neutral atomic species. The experimental results and their interpretation by Surko *et al.* [3] could be viewed as the strongest, albeit indirect, evidence of positron binding to large molecules. This situation has now changed. Many-body theory calculations by Dzuba *et al.* [26] indicated strongly that positrons can be bound by Mg, Zn, Cd, and Hg and, possibly, many other atoms. Recently the variational calculations of Ryzhikh and Mitroy rigorously proved that positrons form bound states with Li atoms, and demonstrated that bound states also exist for Na, Be, Mg, Zn, Cu, and Ag [27]. Molecules are much larger potential wells for the positron, and it seems natural that many of them should be capable of binding positrons.

Ideas about different mechanisms in positron-molecule annihilation were discussed earlier in a number of theoretical [17,23] and experimental [3,22] works. However, there is a need to re-examine this question using a unified approach to the annihilation mechanisms, and define clearly the physical variables which determine the observed annihilation rates. The latter is especially important for the present work, which aims to provide an understanding of a whole variety of phenomena, including the origins of the high values of Z_{eff} for molecules, and their dependence on the chemical composition and positron energy.

II. ANNIHILATION MECHANISMS

In this section a derivation of the positron annihilation rate within a standard scattering theory formalism is presented. I show how to estimate the contributions of the direct and resonant mechanisms, and examine specific features of these mechanisms.

A. General expressions

The effective number of electrons Z_{eff} related to the annihilation rate through Eq. (1) is determined by the positron density on the electrons

$$Z_{\text{eff}} = \int \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) |\Psi_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r})|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_Z d\mathbf{r}, \quad (3)$$

where Z is the number of target electrons, \mathbf{r}_i and \mathbf{r} are the coordinates of the electrons and positron, respectively, and $\Psi_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r})$ is the total wave function of the system. It describes scattering of the positron with initial momentum \mathbf{k} from the atomic or molecular target in the ground state Φ_0 , and is normalized as

$$\Psi_{\mathbf{k}}(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r}) \approx \Phi_0(\mathbf{r}_1, \dots, \mathbf{r}_Z) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (r \gg R_a), \quad (4)$$

where R_a is the radius of the target (atomic units are used throughout). Note that for molecular targets $\Psi_{\mathbf{k}}$ and Φ_0 should, strictly speaking, depend on the nuclear coordinates as well.

Let us first assume that the electron-positron degrees of freedom are completely decoupled from the nuclear motion. The scattering wave function is then determined by the pos-

itron interaction with the charge distribution of the ground-state target and electron-positron correlation interaction (polarization of the target, virtual Ps formation, etc.). Let us denote the corresponding wave function as $\Psi_{\mathbf{k}}^{(0)}$. At positron energies of a few eV the molecule can be excited electronically, and the positron may find itself trapped in electronically excited Feshbach resonance states. This may result in a rapid resonant energy dependence of the $\Psi_{\mathbf{k}}^{(0)}$ wave function. However, at small sub-eV or room-temperature positron energies electron excitations cannot be produced, and $\Psi_{\mathbf{k}}^{(0)}$ behaves smoothly. On the other hand, if the positron affinity of a molecule is positive, the system ‘‘molecule plus positron’’ is capable of forming a stable ‘‘positronic ion,’’ whose lifetime is only limited by positron annihilation. This system will also have a number of excited bound states Φ_{ν} , corresponding to vibrational excitations of the positron-molecule complex. Their typical energies are of the order of 0.1 eV and smaller, as determined by the vibrational spectrum of the molecule.

If we now turn on the coupling V between the electron-positron and nuclear degrees of freedom the total scattering wave function will be given by

$$|\Psi_{\mathbf{k}}\rangle = |\Psi_{\mathbf{k}}^{(0)}\rangle + \sum_{\nu} \frac{|\Phi_{\nu}\rangle \langle \Phi_{\nu}| V |\Psi_{\mathbf{k}}^{(0)}\rangle}{E - E_{\nu} + \frac{i}{2}\Gamma_{\nu}}. \quad (5)$$

The first term on the right-hand side describes direct, or *potential* [28], scattering of the positron by the ground-state molecule. The second term describes positron capture into bound positron-molecule states. Equation (5) has the appearance of a standard perturbation-theory formula. The energy of the system is $E = E_0 + k^2/2$, where E_0 is the target ground-state energy. The energies of the positron-molecule (quasi)bound states Φ_{ν} in the denominator are complex, $E_{\nu} - (i/2)\Gamma_{\nu}$, because these states are, in fact, unstable against positron annihilation with one of the target electrons, and against positron emission, a process inverse to positron capture. Therefore, the total width of state ν is the sum of the annihilation and emission (or capture) widths: $\Gamma_{\nu} = \Gamma_a^{\nu} + \Gamma_c^{\nu}$ [29]. These states manifest themselves as resonances in positron-molecule scattering. They may not give a sizable contribution to the scattering cross section, but, as I show below, they can contribute much to the positron-molecule annihilation rate.

The contribution of a particular resonant state ν to the wave function is proportional to the corresponding capture amplitude $\langle \Phi_{\nu}| V |\Psi_{\mathbf{k}}^{(0)}\rangle$, which also determines the capture width

$$\Gamma_c^{\nu} = 2\pi \int |\langle \Phi_{\nu}| V |\Psi_{\mathbf{k}}^{(0)}\rangle|^2 \frac{k d\Omega_{\mathbf{k}}}{(2\pi)^3} = \frac{k}{\pi} |\langle \Phi_{\nu}| V |\Psi_{\mathbf{k}}^{(0)}\rangle|^2, \quad (6)$$

where the latter formula is valid for the positron *s* wave which dominates at low positron energies (see below). If the positron interaction with vibrations cannot be described by perturbations Eqs. (5) and (6) remain valid, provided we replace the first-order capture amplitudes $\langle \Phi_{\nu}| V |\Psi_{\mathbf{k}}^{(0)}\rangle$ with their nonperturbative values.

The annihilation width of the positron-molecule state Φ_ν is a product of the spin-averaged electron-positron annihilation cross section $\bar{\sigma}_{2\gamma} = \pi r_0^2 c / v$, the positron velocity v , and the density factor

$$\begin{aligned} \Gamma_a^\nu &= \bar{\sigma}_{2\gamma} v \langle \Phi_\nu | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_\nu \rangle \\ &= \pi r_0^2 c \int \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) |\Phi_\nu(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r})|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_Z d\mathbf{r} \\ &\equiv \pi r_0^2 c \rho_{ep}^\nu, \end{aligned} \quad (7)$$

where ρ_{ep}^ν is the average positron density on the target electrons in the ν th bound state. For ground-state positronium, $\rho_{ep}^{\text{Ps}} = (8\pi a_0^3)^{-1}$. One can use this value to estimate the annihilation width of the positron-molecule complex. The presence of many electrons in a large molecule does not lead to an increase of the width, because the positron is spread over a larger volume due to the normalization condition

$$\int |\Phi_\nu(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r})|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_Z d\mathbf{r} = 1.$$

Therefore, using the Ps estimate of the density, one obtains $\Gamma_a^\nu \sim 0.5 \times 10^{-7}$ a.u. ~ 1 μeV , which corresponds to the annihilation lifetime $\tau_a \sim 5 \times 10^{-10}$ s.

To calculate Z_{eff} wave function (5) is substituted into Eq. (3), which yields

$$\begin{aligned} Z_{\text{eff}} &= \langle \Psi_{\mathbf{k}} | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_{\mathbf{k}} \rangle \\ &= \langle \Psi_{\mathbf{k}}^{(0)} | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_{\mathbf{k}}^{(0)} \rangle + (\text{interference terms}) \\ &\quad + \frac{2\pi^2}{k} \sum_{\mu\nu} \frac{A_\mu^* \langle \Phi_\mu | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_\nu \rangle A_\nu}{\left(E - E_\mu - \frac{i}{2}\Gamma_\mu\right) \left(E - E_\nu + \frac{i}{2}\Gamma_\nu\right)}, \end{aligned} \quad (8)$$

where A_ν is the capture amplitude introduced as $\Gamma_c^\nu = 2\pi |A_\nu|^2$ [cf. Eq. (6)]. The terms on the right-hand side correspond to the contributions of direct annihilation, resonant annihilation (i.e., annihilation of the positron captured into the positron-molecule quasibound state), and the interference between the two.

B. Direct annihilation

The direct annihilation term in Eq. (8),

$$Z_{\text{eff}}^{(\text{dir})} = \langle \Psi_{\mathbf{k}}^{(0)} | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Psi_{\mathbf{k}}^{(0)} \rangle, \quad (9)$$

is a smooth function of the positron energy. Let us estimate its magnitude and find its energy dependence at small posi-

tron energies. When the positron is outside the atomic system, $r > R_a$, the wave function $\Psi_{\mathbf{k}}^{(0)}$ contains contributions of the incoming and scattered positron waves,

$$\Psi_{\mathbf{k}}^{(0)}(\mathbf{r}_1, \dots, \mathbf{r}_Z, \mathbf{r}) = \Phi_0(\mathbf{r}_1, \dots, \mathbf{r}_Z) \left[e^{i\mathbf{k}\cdot\mathbf{r}} + f(\Omega) \frac{e^{ikr}}{r} \right], \quad (10)$$

where $f(\Omega)$ is the scattering amplitude. Because of the repulsion from the atomic nuclei the low-energy positron does not penetrate deeply inside the atomic system. Accordingly, the positron annihilates mostly with the outer valence electrons, where the electron and positron densities overlap. This takes place ‘‘on the surface’’ of the atomic system, and Eq. (10) essentially determines the amplitude of finding the positron there. Of course, due to short-range electron-positron correlations the true wave function at small distances cannot be factorized similarly to Eq. (10). The Coulomb interaction between the positron and electron increases the probability of finding both at the same point in space, as required by the δ function in Eq. (3). This effect enhances the annihilation rate [19]. However, since small distances and relatively large interactions are involved, these correlations do not depend on the momentum of the incoming positron at low energies. On the other hand, to participate in the annihilation event the positron must first approach the target, and this is described by Eq. (10). Unlike the short-range correlation effects, the scattering amplitude can be very sensitive to the positron energy. This effect is fully accounted for by Eq. (10), and I use it to evaluate the energy dependence and magnitude of $Z_{\text{eff}}^{(\text{dir})}$.

After substitution of expression (10) into Eq. (9), one obtains

$$\begin{aligned} Z_{\text{eff}}^{(\text{dir})} &= \int \rho(\mathbf{r}) \left[e^{i\mathbf{k}\cdot\mathbf{r}} + f(\Omega) \frac{e^{ikr}}{r} \right] \\ &\quad \times \left[e^{-i\mathbf{k}\cdot\mathbf{r}} + f^*(\Omega) \frac{e^{-ikr}}{r} \right] r^2 dr d\Omega, \end{aligned} \quad (11)$$

where $\rho(\mathbf{r}) \equiv \langle \Phi_0 | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_0 \rangle$ is the electron density in the ground state of the system. The electron density drops quickly outside the atom, and the positron density decreases rapidly inside the atom. Therefore the integration in Eq. (11) should be taken over a relatively thin shell of thickness δR_a enclosing the atomic system. Let us approximate the integration domain by a spherical shell of radius $r = R_a$, where R_a is the typical distance between the positron and the target during the annihilation, comparable to the size of the atom or molecule. For small positron momenta, $kR_a < 1$, Eq. (11) then yields

$$Z_{\text{eff}}^{(\text{dir})} = 4\pi \rho_e \delta R_a \left(R_a^2 + \frac{\sigma_{\text{el}}}{4\pi} + 2R_a \text{Re} f_0 \right), \quad (12)$$

where ρ_e is the electron density in the annihilation range (which can be enhanced due to short-range electron-positron correlations), σ_{el} is the elastic cross section, $\sigma_{\text{el}} = \int |f(\Omega)|^2 d\Omega$, and f_0 is the spherically symmetric part of

the scattering amplitude, $f_0 = (4\pi)^{-1} \int f(\Omega) d\Omega$. For positron interaction with an atom, the latter is simply equal to the s -wave scattering amplitude. Its real part is expressed in terms of the s -wave phase shift δ_0 as $\text{Re} f_0 = \sin 2\delta_0/2k$. The s wave gives a dominant contribution to the cross section σ_{el} at low projectile energies [28]. For $k \rightarrow 0$ it is determined by the scattering length a , $\sigma_{\text{el}} = 4\pi a^2$, as $f(\Omega) = -a$ in this limit. A similar description is also valid for positron scattering from a molecule at small momenta.

Note that the relation between $Z_{\text{eff}}^{(\text{dir})}$ and elastic scattering given by Eq. (12) could also be derived by matching the true many-body wave function of the positron-target system at low energy ($E \approx 0$) with the asymptotic form [Eq. (10)]. In this case R_a will be the matching radius, and the factor before the brackets will remain a free atomic-sized parameter. However, even in form (12) the electron density ρ_e and the overlap δR_a are effective parameters, and the accurate value of the prefactor can only be found by comparison with numerical calculations (see Sec. III A). Nevertheless, Eq. (12) is very useful for an analysis of direct annihilation. The three terms in brackets are due to the incoming positron plane wave, the scattered wave, and the interference term, respectively; cf. Eqs. (10) and (11). Even if the cross section σ_{el} is zero or very small, as in the case of a Ramsauer-Townsend minimum, the annihilation rate $Z_{\text{eff}}^{(\text{dir})}$ is nonzero. Its magnitude is determined by the effective annihilation radius R_a , electron density ρ_e and δR_a , which gives $Z_{\text{eff}}^{(\text{dir})} \sim 1-10$, since the quantities involved have ‘‘normal,’’ atomic-sized values.

Equation (12) shows that the annihilation rate for slow positrons is greatly enhanced if the scattering cross section is large. This occurs when the scattering length is large, because the positron-target interaction supports a low-lying virtual s level ($a < 0$) or a weakly bound s state ($a > 0$) [28]. Their energies, $\varepsilon_0 = \pm 1/2a^2$, respectively, must be much smaller than typical atomic energies, $|\varepsilon_0| \ll 1$ Ry. For $|a| \gg R_a$ the scattering cross section at low energies is much greater than the geometrical size of the target. This effect leads to a strong enhancement of $Z_{\text{eff}}^{(\text{dir})}$ [17–19]. Theoretically, this gives the possibility of infinitely large cross sections and annihilation rates at zero positron energy, if $|a| \rightarrow \infty$. However, for nonzero momenta the s -wave cross section does not exceed the unitarity limit $\sigma_{\text{el}} = 4\pi/k^2$ (for the s wave). This fact puts a bound on the enhancement of $Z_{\text{eff}}^{(\text{dir})}$. For example, for thermal positrons with $k^2/2 \sim k_B T$ at room temperature ($k \sim 0.05$ a.u.) we obtain $Z_{\text{eff}}^{(\text{dir})} \sim 10^3$ from Eq. (12). Consequently, much higher values of Z_{eff} cannot be produced by the direct annihilation mechanism. A more detailed discussion of this point and illustrations of the validity of Eq. (12) are presented in Sec. III A.

C. Resonant annihilation

Unlike the direct annihilation term, the interference and the resonant terms on the right-hand side of Eq. (8) are rapidly varying functions of energy. The energy scale of this variation is given by the mean spacing D between the resonances. If the resonances are due to vibrational excitations of a single mode of the positron-molecule complex, then D

$= \omega$, with $\omega \lesssim 0.1$ eV for a typical vibrational frequency. In a complex molecule the positron attachment energy is sufficient for excitation of several modes, and D can be much smaller. To describe the annihilation rates observed in experiments with nonmonochromatic, e.g., thermal, positrons, one needs to average the interference and resonance terms over an energy interval ΔE which contains many resonances:

$$\frac{1}{\Delta E} \int_{\Delta E} dE \left[2 \sqrt{\frac{2\pi^2}{k}} \text{Re} \sum_{\nu} \frac{\langle \Psi_{\mathbf{k}}^{(0)} | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_{\nu} \rangle A_{\nu}}{E - E_{\nu} + \frac{i}{2} \Gamma_{\nu}} + \frac{2\pi^2}{k} \sum_{\mu\nu} \frac{A_{\mu}^* \langle \Phi_{\mu} | \sum_{i=1}^Z \delta(\mathbf{r} - \mathbf{r}_i) | \Phi_{\nu} \rangle A_{\nu}}{\left(E - E_{\mu} - \frac{i}{2} \Gamma_{\mu} \right) \left(E - E_{\nu} + \frac{i}{2} \Gamma_{\nu} \right)} \right]. \quad (13)$$

Upon averaging the first interference term vanishes. In the second resonance term the diagonal items in the sum ($\mu = \nu$) dominate. Averaging is then reduced to the integral over the Breit-Wigner resonant profiles. The number of resonances within ΔE is $\Delta E/D$. Therefore, the total annihilation rate is the sum of the direct and resonant contributions,

$$Z_{\text{eff}} = Z_{\text{eff}}^{(\text{dir})} + Z_{\text{eff}}^{(\text{res})}, \quad (14)$$

with the resonant contribution given by

$$Z_{\text{eff}}^{(\text{res})} = \frac{2\pi^2}{k} \left\langle \frac{\rho_{ep}^{\nu} \Gamma_c^{\nu}}{D[\Gamma_a^{\nu} + \Gamma_c^{\nu}]} \right\rangle, \quad (15)$$

where the angular brackets stand for averaging over the resonances, and $\Gamma_{\nu} = \Gamma_a^{\nu} + \Gamma_c^{\nu}$ substituted for the total width. Below I will show that the resonant term in Eq. (14) can be much greater than the direct one, and very high Z_{eff} values can be achieved.

It is easy to see that the resonant contribution could also be derived from standard resonant scattering theory developed originally to describe neutron scattering via compound nucleus resonances (Ref. [28], Chap. 18). The maximal s -wave capture cross section is given by $\sigma = \pi \lambda^2 \equiv \pi k^{-2}$. The true capture cross section is smaller than σ , because the capture takes place only when the positron energy matches the energy of the resonance. For positrons with finite energy spread (e.g., thermal ones), the capture cross section is then $\sigma_c \sim (\Gamma_c/D)\sigma$, where D is the mean energy spacing between the resonances. More accurately, $\sigma_c = (2\pi\Gamma_c/D)\sigma$ [28]. If we are concerned with the annihilation process, the capture cross section must be multiplied by the probability of annihilation, $P_a = \Gamma_a/(\Gamma_c + \Gamma_a)$, which gives the energy-averaged resonance annihilation cross section

$$\sigma_a = \frac{2\pi^2}{k^2} \frac{\Gamma_a \Gamma_c}{D(\Gamma_c + \Gamma_a)}, \quad (16)$$

where averaging over resonances similar to that in Eq. (15) is assumed. By comparison with Eqs. (2) and (7), the resonant contribution to Z_{eff} [Eq. (15)], is recovered.

The way Eq. (15) has been derived implies that the positrons are captured in the s wave. Otherwise, an additional factor of $(2l+1)$, where l is the positron orbital momentum, appears in the formula [28]. At low positron energies the capture widths behave as

$$\Gamma_c \propto (kR)^{2l+1} \quad (17)$$

for resonances formed by positron capture with the orbital momentum l [28] (R is the typical radius of the target). So s -wave capture indeed dominates in the resonant annihilation of slow positrons. At higher energies contributions of several lowest partial waves should be added into $Z_{\text{eff}}^{(\text{res})}$.

Let us estimate the rate of resonant annihilation and compare it with the maximal direct contribution $Z_{\text{eff}}^{(\text{dir})} \sim 10^3$ for room-temperature positrons. The typical annihilation widths for positron-molecule (quasi)bound states are very small, $\Gamma_a^v \sim 1 \mu\text{eV}$ (see Sec. II A). If one assumes that the positron capture width is much greater,

$$\Gamma_c^v \gg \Gamma_a^v, \quad (18)$$

the total width $\Gamma_v \approx \Gamma_c^v$ cancels the capture width in Eq. (15), and the resonant contribution is given by

$$Z_{\text{eff}}^{(\text{res})} = \frac{2\pi^2}{k} \left\langle \frac{\rho_{ep}^v}{D} \right\rangle = \frac{2\pi^2}{k} \rho_{ep} \rho(E_v). \quad (19)$$

In the last equality I use the fact that electron-positron degrees of freedom are almost unaffected by the vibrational motion of the nuclei. Hence for a given molecule the positron density on the target electrons, ρ_{ep} , is the same for different vibrational resonances. I have also introduced the density of resonances $\rho(E_v) = D^{-1}$, where $E_v = \varepsilon_A + \varepsilon$ is the vibrational excitation energy due to positron-molecule binding. Equation (19) shows that for $\Gamma_c > 1 \mu\text{eV}$ the contribution of the resonant mechanism is *independent* of the capture width, and is determined by the density of positron-molecule resonant states populated by positron capture. Suppose that only a single mode with $D \sim 0.1 \text{ eV}$ is excited. Equation (19) then yields $Z_{\text{eff}}^{(\text{res})} \sim 4 \times 10^3$, if I use the estimates $\rho_{ep} = \rho_{ep}^{\text{Ps}}$, and $k = 0.05$ for room-temperature positrons.

The resonance spacing D cannot be smaller than the widths of the resonances, which are limited by the annihilation width Γ_a . Thus one can obtain an upper estimate of the resonant annihilation rate from Eq. (15) by putting $\Gamma_c \approx \Gamma_a \sim 0.5 \times 10^{-7} \text{ a.u.}$, and $D \sim 2\pi\Gamma_c$, which gives the maximal possible capture cross section σ . These estimates yield $Z_{\text{eff}}^{(\text{res})} \sim 5 \times 10^7$ at room temperature (cf. $Z_{\text{eff}} = 7.5 \times 10^6$ for $\text{C}_{12}\text{H}_{22}\text{O}_4$ [15]). This theoretical maximum of $Z_{\text{eff}}^{(\text{res})}$ corresponds to the unitarity limit of the s -wave capture cross section. However, this estimate of Z_{eff} is not trivial. The resonance mechanism shows that such large cross sections can be achieved for the annihilation process, in spite of the fact that it is suppressed by the quantum-electrodynamic factor $\pi r_0^2 c = \pi/c^3 \sim 10^{-6}$, in atomic units [see Eq. (2)].

Equation (19) predicts unusual low-energy threshold behavior $Z_{\text{eff}}^{(\text{res})} \propto 1/k \propto 1/\sqrt{T}$ (the latter for thermal positrons). In a standard situation the cross section of an inelastic process involving a slow projectile in the initial state behaves as $\sigma \propto 1/k$. This dependence is characteristic of the s -wave scattering, which dominates at low projectile energies, and is valid in the absence of long-range forces between the target and the projectile. It is known as the “ $1/v$ ” law, and its examples are numerous: from the (n, γ) nuclear reaction to dissociative electron attachment to molecules, where it is observed below 1 meV [30]. Therefore, one would expect the positron annihilation cross section to behave as $\sigma_a \propto 1/k$. Accordingly, Z_{eff} , which is proportional to the annihilation rate, is expected to be constant at low positron energies.

The anomalous threshold dependence of Eq. (19) clearly contradicts this general statement. This “puzzle” is easily resolved if we recall condition (18) that led to Eq. (19). For very low positron momenta the s -wave capture width behaves as $\Gamma_c \propto kR$, so that Eq. (18) is clearly violated, and the resonant contribution in Eq. (14) becomes constant as $k \rightarrow 0$. However, at higher positron energies the $1/k$ behavior of Z_{eff} may be observed. This dependence corresponds to the $1/\varepsilon$ drop of the cross section which is reported in some electron attachment experiments (see, e.g., Ref. [31]).

The fact that positron-molecule resonances give a large contribution to the annihilation rate, as compared to the direct annihilation, does not mean that they also contribute much to the elastic scattering cross section. In analogy with Eq. (16), the resonant contribution to the elastic scattering is given by

$$\sigma_{\text{el}}^{(\text{res})} = \frac{2\pi^2}{k^2} \frac{\Gamma_c^2}{D(\Gamma_c + \Gamma_a)}, \quad (20)$$

and for $\Gamma_c \ll D$ it is much smaller than the direct, or potential, scattering cross section.

III. ILLUSTRATIONS AND COMPARISON WITH EXPERIMENT

A. Effect of virtual or weakly bound states on direct annihilation

If low-energy positron scattering is dominated by the presence of a virtual or weakly bound state at $\varepsilon_0 = \pm \kappa^2/2$, the corresponding cross section has the form (for scattering by a short-range potential [28])

$$\sigma_{\text{el}} = \frac{4\pi}{\kappa^2 + k^2}, \quad (21)$$

where $\kappa = a^{-1}$. According to Eq. (12) a similar maximum should appear in the momentum dependence of the annihilation rate. Its magnitude at $k=0$ can be arbitrarily large if $\kappa \rightarrow 0$ ($|a| \rightarrow \infty$), which corresponds to a level at zero energy. However, for nonzero momenta the maximal cross section is finite, $\sigma_{\text{el}} \sim 4\pi/k^2$, which corresponds to the unitarity limit for the s -wave cross section.

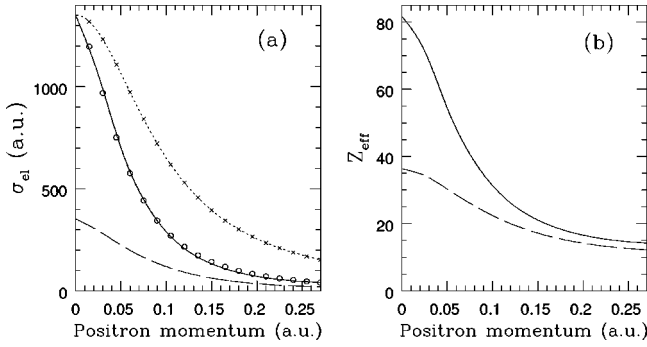


FIG. 2. Elastic scattering cross section σ_{el} (a) and annihilation rates Z_{eff} (b) for Ar (dashed curves) and Kr (solid curves), as calculated in Ref. [33]. Also shown in (a) are the analytical approximations of σ_{el} for Kr by the short-ranged potential formula (21) (dotted line with crosses), and the modified effective range formula (23), which accounts for the dipole polarization of the target (open circles). Here I have used the calculated value of $a = -10.4$ a.u., an experimental dipole polarizability $\alpha = 16.74$ a.u. [34], and $C = 0.4$ obtained from the s -wave phase shift of Ref. [33]. Note that the modified effective range formula (open circles) gives an accurate description of the cross section shown by the solid curve.

Real atomic and molecular targets have nonzero electric dipole polarizabilities α , which give rise to the long-range polarization potential $-\alpha/2r^4$ for the positron. Its effect is taken into account by the modified effective-range formula for the s -wave phase shift [32],

$$\tan \delta_0 = -ak \left[1 - \frac{\pi\alpha k}{3a} - \frac{4\alpha k^2}{3} \ln \left(\frac{C}{4} \sqrt{\alpha k} \right) \right]^{-1}, \quad (22)$$

$$\sigma_{el} = \frac{4\pi a^2}{\left[1 - (\pi\alpha k/3a) - (4\alpha k^2/3) \ln \left(\frac{C}{4} \sqrt{\alpha k} \right) \right]^2 + a^2 k^2}, \quad (23)$$

the latter formula being valid when the scattering length is large and the s -wave scattering dominates at small k . In Eqs. (22) and (23) C is a dimensionless positive constant. Note that, for $\alpha = 0$, Eq. (21) is immediately recovered. The polarization potential modifies the behavior of the cross section at low energies. For example, it leads to a more rapid decrease of the cross section for $a < 0$, $\sigma_{el} = 4\pi a^2 [1 + 2\pi\alpha k/3a + O(k^2 \ln k)]$. However, this does not change the estimates of the maximal values of Z_{eff} that could be produced in direct annihilation.

To illustrate the relation between direct annihilation and elastic scattering, and the enhancement of both due to the presence of a low-lying virtual level, let us compare the behaviors of Z_{eff} and σ_{el} for Ar and Kr. The results shown in Fig. 2 were obtained within the polarized-orbital method [33], which takes into account the polarization of the target by the positron. These calculations yield large negative values of the scattering length for Ar, Kr, and Xe (see Table I), indicating the presence of positron-atom virtual levels formed due to strong positron-atom attraction. The increase of $|a|$ correlates with the increase of the dipole polarizability

TABLE I. Scattering lengths and fitting parameters for the relation between $Z_{eff}^{(dir)}$ and σ_{el} [Eq. (12)].

Atom or molecule	a (a.u.)	R_a (a.u.)	$4\pi\rho_e\delta R_a$ (a.u.)
He	-0.52^a	3.9	0.21
Ne	-0.61^a	5.0	0.23
Ar	-5.30^a	4.3	0.42
Kr	-10.4^a	4.2	0.41
Xe	-45.3^a	4.2	0.41
C_2H_4	-18.5^b	4.4	3.0

^aCalculated in Ref. [33].

^bObtained from the calculations of da Silva *et al.* [8].

in these atoms. Similar values of a have been obtained in the many-body theory calculations of Dzuba *et al.* [19]. Figure 2 shows that both σ_{el} and Z_{eff} are enhanced at low momenta due to the presence of the virtual s levels. This effect is stronger for Kr, which has a greater absolute value of the positron scattering length. As illustrated by Fig. 2(a) for Kr, Eq. (23) provides a good description of the cross section at small k . The visible difference between Z_{eff} and σ_{el} in Fig. 2 is due to the background given by the energy-independent term R_a^2 in Eq. (12).

Figure 3 provides a direct comparison between Z_{eff} and the right-hand side of Eq. (12), and shows that this relation is

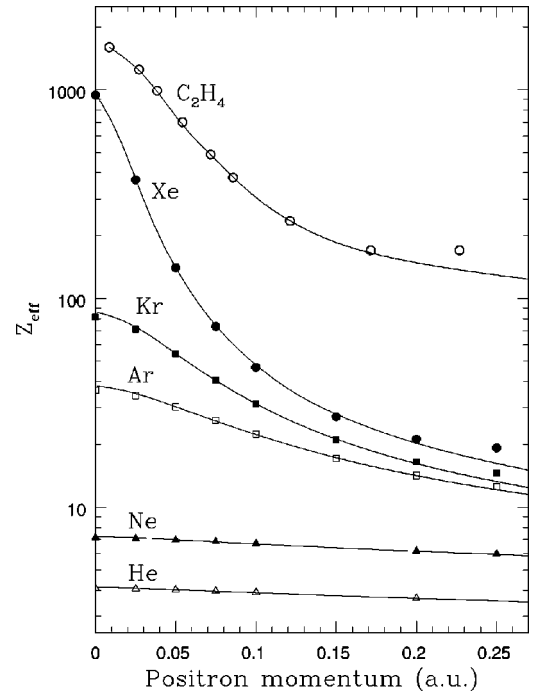


FIG. 3. Relation between Z_{eff} due to direct annihilation and the elastic scattering cross section. Calculated Z_{eff} values for He (open triangles), Ne (solid triangles), Ar (open squares), Kr (solid squares), and Xe (solid circles) [33], and C_2H_4 (open circles) [8] are compared with the predictions of Eq. (12), shown by solid curves. In the latter I have used the scattering cross sections and amplitudes calculated in the same theoretical papers, and considered R_a and the prefactor $4\pi\rho_e\delta R_a$ as fitting parameters.

valid at low positron energies. The comparison is based on the polarized-orbital method results for the noble-gas atoms [33], and the values of Z_{eff} and σ_{el} obtained for the ethylene molecule (C_2H_4) by the Schwinger multichannel method [8]. In this comparison I have considered R_a and the prefactor $4\pi\rho_e\delta R_a$ in Eq. (12) as fitting parameters. Their values are listed in Table I together with the values of a obtained in those calculations. Note that the theoretical results used to produce this plot are not necessarily “exact” or accurate (although, experimental data confirm that they are reasonable [7,20]). It follows from the derivation that Eq. (12) holds for any calculation, as long as the same wave function is used in the scattering and annihilation calculations [35].

In agreement with the estimates made in Sec. II B, Fig. 3 shows that direct annihilation is indeed strongly enhanced by the presence of low-lying virtual levels. Nevertheless, even for targets with very large scattering lengths, such as Xe or C_2H_4 , the annihilation rates do not exceed $Z_{\text{eff}} \sim 10^3$ for room-temperature positron momenta (0.05 a.u.).

Direct annihilation is the only annihilation mechanism for atoms and molecules which do not form bound states with positrons. It will also dominate for small molecules which do form a weakly bound state with the positron, but whose vibrational frequencies are high. In this case the energy $\varepsilon_A + \varepsilon$ is simply insufficient for the excitation of the resonant quasibound states at low impact positron energies ε .

For large molecules the difference between the resonant and direct mechanisms is probably most obvious when one compares the experimental values of Z_{eff} for alkanes and perfluorinated alkanes shown in Fig. 1. The large annihilation rates of the alkane molecules with more than two carbon atoms cannot be explained by direct annihilation. They also display a very rapid increase with the size of the molecule, which is typical of resonant annihilation. On the other hand, the Z_{eff} values of the perfluorinated alkanes remain comparatively small, in spite of their softer vibrational spectra. Thus one is led to conclude that the resonant mechanism is switched off for them. The latter is explained by the very weak attraction between the positron and fluorine atoms [7], insufficient to provide positron-molecule binding.

Let us examine the effect of fluorination on Z_{eff} for the lightest molecule of the series, methane. The experimental data at room temperature are $Z_{\text{eff}} = 158.5, 715, 411, 127,$ and 38 for $\text{CH}_4, \text{CH}_3\text{F}, \text{CH}_2\text{F}_2, \text{CHF}_3,$ and CF_4 , respectively (data from Refs. [7,12] normalized to the given value for methane). These values are small enough to be accounted for by the direct mechanism. Within its framework the increase and subsequent drop of Z_{eff} could be explained by the existence of a loosely bound state for the positron on methane, which turns into a virtual level as the number of substitute fluorine atoms increases [36]. In terms of the κ parameter this would mean that κ is small and positive for CH_4 , and then goes through zero, and becomes negative upon fluorination. Accordingly, both the cross section and the annihilation rate peak for the molecule with the smallest absolute value of κ , namely, CH_3F . This picture is considered in Ref. [7] in more detail using the zero-range potential model for positron-molecule interaction.

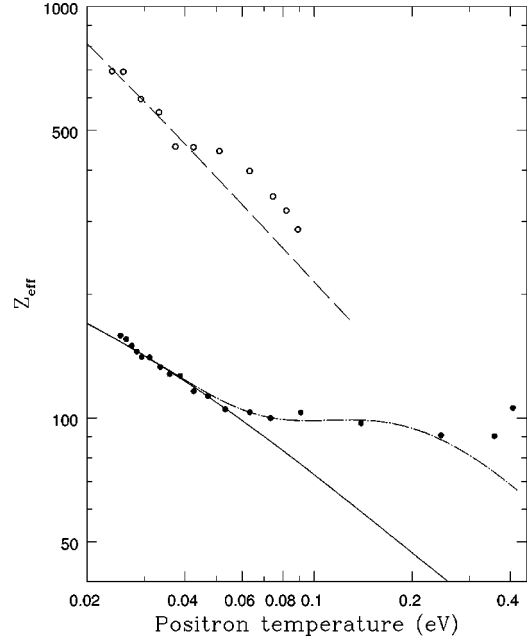


FIG. 4. Annihilation rates for methane and fluoromethane. Experimental data for CH_4 (solid circles) and CH_3F (open circles) [7] have been normalized to $Z_{\text{eff}} = 158.5$ for methane at room temperature. Thermal-averaged direct annihilation fits obtained from Eqs. (12) and (23) using $4\pi\rho_e\delta R_a = 1, R_a = 4, C = 1, \alpha = 17.6$ a.u. are shown for CH_4 ($\kappa = 0.045$, solid curve) and CH_3F ($\kappa = 0.01$, dashed curve). Also shown for methane is the sum of the direct contribution and that of the first vibrational A_1 resonance at $\varepsilon_\nu = 0.33$ eV, obtained using $\rho_{ep}^\nu = 0.25\rho_{ep}^{\text{Ps}}$ [Eq. (25)] (chain curve).

Besides having a larger value of Z_{eff} , the molecule with a smaller $|\kappa|$ (i.e., larger $|a|$) should have a more rapid dependence of the annihilation rate on the positron energy, cf. Fig. 3. If the experiment is done with thermal positrons this should manifest in a stronger temperature dependence of the Maxwellian average of $Z_{\text{eff}}(k)$,

$$\bar{Z}_{\text{eff}}(T) = \int_0^\infty \frac{e^{-k^2/2k_B T}}{(2\pi k_B T)^{3/2}} Z_{\text{eff}}(k) 4\pi k^2 dk, \quad (24)$$

on the positron temperature T . The overbar is usually omitted, as it is clear from the context whether one is dealing with $Z_{\text{eff}}(k)$ at a specific positron momentum, or with a thermal average $\bar{Z}_{\text{eff}}(T)$. The temperature dependences of the annihilation rates for methane and fluoromethane measured in Ref. [7] are shown in Fig. 4. Also shown are low-temperature theoretical fits obtained using Eqs. (12), (23), and (24). Their parameters are given in the caption.

The dipole polarizability of CH_3F $\alpha = 16.1$ a.u. is close to that of methane, $\alpha = 17.6$ a.u., and I use the latter for both molecules. The constant C appears in Eqs. (22) and (23) under the logarithm, and the result is not very sensitive to it, so $C = 1$ has been chosen. The value of the characteristic radius $R_a = 4$ a.u. is similar to those for noble gas atoms and ethylene (Table I), and the prefactor $4\pi\rho_e\delta R_a = 1$ is between those for noble-gas atoms and C_2H_4 . Of course, the number of independent parameters ($a, C, R_a,$ and

$4\pi\rho_e\delta R_a$) is too large to enable their unique determination from the experimental data. However, the fits clearly demonstrate that very different $Z_{\text{eff}}(T)$ curves can be obtained *only* due to different κ values ($\kappa=0.045$ and 0.01 for CH_4 and CH_3F , respectively). These values imply that both molecules have bound states with the positron. The binding energy for CH_4 is $\varepsilon_A=\kappa^2/2=1.0\times 10^{-3}$ a.u.= 0.028 eV, and the binding energy corresponding to $\kappa=0.01$ is just 1 meV. There is a large uncertainty in the latter value, because measurements performed at and above room temperature, $T=0.0253$ eV, are not really sensitive to such small κ . This can be seen, e.g., from Eq. (21), which becomes κ independent for $\kappa\ll k$. Zero-range model calculations presented in Ref. [7] show that the last three members of the fluoromethane sequence have negative κ , corresponding to virtual levels with increasing energies. This causes the decrease of their Z_{eff} values.

As seen in Fig. 4, Eq. (12) for the direct annihilation combined with the modified effective range formula (23) works well in the low-energy part of the graph. However, the data for methane clearly show an abrupt departure from this law at higher T , and the formation of some kind of a plateau in $Z_{\text{eff}}(T)$. In principle, one could think that this is due to contributions of higher partial waves, not included in σ_{el} [Eq. (23)]. However, their contribution has been included via the R_a term of Eq. (12). Also, the contributions of higher partial waves to Z_{eff} emerge as ε^l , which is a manifestation of the Wigner threshold law [28]. For thermally averaged rates this corresponds to T^l . Thus it cannot be responsible for this sudden feature.

On the other hand, if the methane molecule forms a bound state with the positron, the system can also have vibrationally excited positron-molecule resonant states. The positron bound state on CH_4 must belong to the A_1 symmetry type of the molecule. Since the positron s wave dominates at low energies, its capture into the A_1 state can result in an excitation of A_1 vibrational modes of the molecule. The frequency of this mode for methane is $\omega=2916\text{ cm}^{-1}=0.361$ eV [37]. Assuming that the positron binding does not change this frequency much, the lowest vibrationally excited positron-molecule resonance will occur at $\varepsilon=\omega-\varepsilon_A\approx 0.33$ eV.

It is easy to estimate the contribution of a single narrow vibrational resonance located at positron energy ε_ν to the thermally averaged Z_{eff} [38],

$$\Delta Z_{\text{eff}}(T)=\frac{8\pi^3\rho_{ep}^{\nu}\Gamma_c^{\nu}}{\Gamma_a^{\nu}+\Gamma_c^{\nu}}\frac{e^{-\varepsilon_\nu/k_B T}}{(2\pi k_B T)^{3/2}}\approx 8\pi^3\rho_{ep}^{\nu}\frac{e^{-\varepsilon_\nu/k_B T}}{(2\pi k_B T)^{3/2}}, \quad (25)$$

the latter formula valid for $\Gamma_c^{\nu}\gg\Gamma_a^{\nu}$, which implies that the resonance has a capture width greater than $1\mu\text{eV}$. Figure 4 shows the effect of the lowest vibrational A_1 resonance at $\varepsilon_\nu=0.33$ eV on Z_{eff} for methane (chain curve). Its onset is indeed quite rapid, due to the exponent in Eq. (25), which makes $\Delta Z_{\text{eff}}(T)$ very small for $k_B T<\varepsilon_\nu$. To fit the experimental data the density ρ_{ep}^{ν} is chosen to be 25% of ρ_{ep}^{Ps} . One could expect that for a weakly bound state ($\varepsilon_A=0.028$ eV),

where the positron spends most of its time outside the molecule, its density on the electrons is reduced below that of Ps (binding energy 6.8 eV) [39].

B. Resonant annihilation: molecular vibrations and temperature dependence

I. Vibrations

Equation (19) derived in Sec. II C shows that the annihilation rate due to positron capture into resonances is determined by the level density of these quasibound vibrationally excited states of the positron-molecule complex. This density depends on the excitation energy available, as defined by the positron kinetic energy and positron affinity, $E_\nu=\varepsilon_A+\varepsilon$, and also on the structure of the molecular vibrational spectrum. Suppose that the molecule possesses a particular symmetry, which is true for most of the molecules where positron annihilation has been studied so far [4]. The electronic ground-state wave function of the molecule is usually non-degenerate and invariant under all symmetry transformations. Let us call this symmetry type A . Depending on the actual symmetry of the molecule this can be A_1 , A_g , or A_{1g} . If the positron can be bound by such molecule, the electron-positron part of the wave function of the positron-molecule complex will also be fully symmetric, i.e., of A symmetry type.

Now consider the capture of a continuous spectrum positron into the bound positron-molecule state. At low positron energies this process is dominated by the incident positron s wave, higher partial waves being suppressed as $(kR)^{2l}$, compared to the s wave [cf. Eq. (17)]. As a result, the electron-positron part of the wave function of the initial (molecule and s -wave positron) and final (bound positron-molecule complex) states of the capture process are characterized by the same full molecular symmetry A . This imposes a selection rule on the nuclear vibrations which can be excited during the capture process. They must also belong to the A symmetry type.

Therefore, the selection rule limits the spectrum of possible vibrationally excited resonances which could in principle be formed. It allows arbitrary excitations and combinations of the A modes. It also allows overtones and combinations of the other symmetry types, provided such excitations contain the A symmetry type, i.e., the (symmetric) product of the symmetry types involved contains A among its irreducible representations [28]. This does not mean that all such vibrations will contribute to the density factor $\rho(E_\nu)$ in Eq. (19) for Z_{eff} . Some of them may have extremely weak coupling to the electron-positron degrees of freedom, with capture widths much smaller than $1\mu\text{eV}$. In this case they will be effectively decoupled from the positron capture channel, and hence, will not contribute to Z_{eff} . Of course, this can only be found out by doing detailed calculations for specific molecules.

Nevertheless, it is instructive to compare Eq. (19) with experimental data. This comparison enables one to extract the effective mean spacing D between the positron-molecule resonances. For experiments with thermal positrons Eq. (19)

TABLE II. Annihilation rates and vibrational frequencies of molecules.

Molecule	Formula	$Z_{\text{eff}}^{\text{a}}$	D^{b} (cm ⁻¹)	Symmetry	Frequencies ^c (cm ⁻¹)
Carbon tetrachloride	CCl ₄	9 530	473	A ₁	459
Butane	C ₄ H ₁₀	11 300	399	A _g	429, 837, 1057, ...
Cyclohexane	C ₆ H ₁₂	20 000	226	A _{1g}	384, 802, 1158, ...
Pentane	C ₅ H ₁₂	37 800	119	A ₁	179, 401, 863, ...
Carbon tetrabromide	CBr ₄	39 800	113	A ₁	269
Hexachloroethane	C ₂ Cl ₆	68 600	65.7	A _{1g}	164, 431, 976
Hexane	C ₆ H ₁₄	120 000	37.6	A _g	305, 371, 901, ...
Heptane	C ₇ H ₁₆	242 000	18.6		

^aExperimental values obtained for room-temperature positrons in the trap (Ref. [4]).

^bEffective spacing for the resonances in $Z_{\text{eff}}^{\text{(res)}}$ [Eq. (26)], corresponding to experimental data.

^cLowest molecular vibrational frequencies of the given symmetry from Ref. [37].

must be averaged over the Maxwellian positron momenta distribution:

$$Z_{\text{eff}}^{\text{(res)}} = \frac{2\pi^2 \rho_{ep}}{D} \left\langle \frac{1}{k} \right\rangle_T = \frac{2\pi^2 \rho_{ep}}{D} \left(\frac{2}{\pi k_B T} \right)^{1/2}. \quad (26)$$

Let us use the Ps value, $\rho_{ep} = 1/8\pi$, to estimate the electron-positron density, and apply Eq. (26) to simple symmetric molecules with $Z_{\text{eff}} \gtrsim 10^4$, where resonant annihilation must be the dominant mechanism. The effective spacings $D = 4.51 \times 10^6 / Z_{\text{eff}}$ (in cm⁻¹) obtained from the experimental Z_{eff} values measured with room-temperature positrons [4] are listed in Table II. They are compared with the low-frequency vibrational modes of the A symmetry type of these molecules taken from Ref. [37]. As discussed above, vibrations of the A symmetry type also occur in overtones and combinations of other modes. However, their frequencies scale with the size and chemical composition of the molecule in a way similar to the A modes, and the A mode frequencies listed in the table are representative of the lower vibrational modes on the whole.

For molecules with moderate Z_{eff} at the top of the table, such as CCl₄, the effective resonance spacing D is comparable to the frequencies of single modes. With the increase of the size of the molecule (alkanes), or masses of the constituents (e.g., CBr₄), the vibrational modes are softened, and the number of low-frequency modes increases. At the same time one can expect that the positron binding energy increases for these molecules. These effects, and especially the increase of the number of modes, facilitate multimode excitations, whose density is much greater than the level density of the individual modes. Accordingly, we see that D becomes much smaller than the frequencies of the individual modes at the bottom of the table.

In the simplest model this effect can be estimated as follows. Suppose the vibrational modes in question are characterized by some typical frequency ω , and the molecule has N_v such modes. Suppose, the positron binding energy is $\varepsilon_A = n\omega$, where n is the number of vibrational quanta excited due to positron binding. If we neglect the small kinetic energy of the positron, $E_v \approx \varepsilon_A$, the total number of various vibrational excitations at energy E_v is given by $(N_v + n$

$-1)!/[n!(N_v - 1)!]$ (the number of ways to distribute n vibrational quanta among N_v modes). For large molecules ε_A remains finite, whereas N_v increases linearly with the size of the molecule, the total number of vibrational modes being $3N - 6$, where N is the number of atoms. Therefore, the number of vibrational excitations available, and the density of the resonant vibrational spectrum, increase as $(N_v)^n \propto N^n$. Such a rapid increase is indeed observed for alkanes and aromatic hydrocarbons; see Fig. 1. The effective numbers of vibrational modes excited in the capture process, $n = 6.1$ and 8.2 , respectively, is compatible with the positron binding energy of few tens of eV. For example, if I use the lowest A_g mode frequency of hexane (Table II), the positron affinity is $\varepsilon_A \sim 6\omega \approx 0.25$ eV. This number looks reasonable, compared with positron binding energies on single atoms, e.g., $\varepsilon_A = 0.08, 0.15,$ and 0.38 for Be, Cu, and Mg, respectively [27,39].

Apart from the rapid growth, Z_{eff} for alkanes shows clear signs of saturation, when the number of carbon atoms becomes greater than 8 or 10. Apparently, this takes place well before the unitarity limit derived in Sec. II C is reached. This behavior can be understood if we recall that Eq. (19) is valid only when the capture width Γ_c is greater than the annihilation width Γ_a . With the increase of the number of vibrational modes their coupling to the electron-positron degrees of freedom decreases. This coupling is represented by Γ_c , and for small capture widths, $\Gamma_c < \Gamma_a$, $Z_{\text{eff}}^{\text{(res)}}$ from Eq. (15) is estimated as

$$Z_{\text{eff}}^{\text{(res)}} \approx \frac{2\pi^2}{k} \left\langle \frac{\rho_{ep} \Gamma_c^v}{D \Gamma_a^v} \right\rangle = \frac{2\pi c^3}{k} \left\langle \frac{\Gamma_c^v}{D} \right\rangle, \quad (27)$$

where Eq. (7) is used together with $r_0 = c^{-2}$, in atomic units. The decrease of Γ_c is a simple consequence of sum rules, because the total strength of positron coupling is distributed among the larger number of possible vibrational excitations. In this regime Γ_c is proportional to D , hence the increase of $Z_{\text{eff}}^{\text{(res)}}$ related to the increase of the density of vibrational excitation spectrum stops. The relation $\Gamma_c \propto D$ which characterizes this regime is well known in neutron capture into compound resonances [40]. It takes place in complex atomic

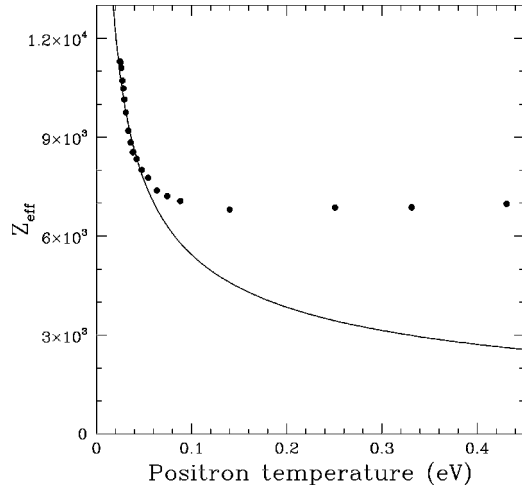


FIG. 5. Dependence of Z_{eff} on positron temperature for butane, C_4H_{10} . Solid circles show experimental data [7], normalized at room temperature to $Z_{\text{eff}} = 11300$ [4]. The solid curve is the $1/\sqrt{T}$ dependence [Eq. (26)], with $\rho_{ep} = \rho_{ep}^{\text{Ps}}$, and effective resonance spacing $D = 1.90 \times 10^{-3}$ a.u. = 417 cm^{-1} .

spectra, e.g., in rare earths, where the oscillator strengths are distributed among very large numbers of transitions [41]. It also emerges in the unimolecular reaction treatment of dissociative electron attachment [21], where it is responsible for very large lifetimes (i.e., small state widths) of transient molecular anions.

2. Dependence on the positron energy or temperature

Let us now look at the energy dependence of the resonant annihilation rate. At very small positron energies $Z_{\text{eff}}^{(\text{res})}$ must be constant (see the discussion at the end of Sec. II C). However, as soon as the s -wave capture width becomes greater than $1 \mu\text{eV}$, the corresponding annihilation rate shows a $1/k \sim \varepsilon^{-1/2}$ dependence on positron energy, as predicted by Eq. (19). For a thermally averaged rate this is described by Eq. (26). Figure 5 presents a comparison between the $1/\sqrt{T}$ law and the experimental temperature dependence of Z_{eff} for C_4H_{10} [7]. This molecule has $Z_{\text{eff}} \sim 10^4$. Within the present theoretical framework this large value must be due to the resonant annihilation process.

The theory and experiment agree well at low temperatures. One may notice that the measured Z_{eff} show a slightly steeper rise toward small T . However, the difference is not large, both in relative and absolute terms. It could be explained by a direct contribution $Z_{\text{eff}}^{(\text{dir})}$ in Eq. (14), which peaks sharply at small energies, if the positron-molecule scattering length is large (see Sec. III A). In spite of the dominance of the resonant contribution, $Z_{\text{eff}}^{(\text{res})} \sim 10^4$ for butane, the addition of $Z_{\text{eff}}^{(\text{dir})} \sim 10^3$ at small positron energies would still be noticeable.

A more pronounced feature of the experimental data, which is not accounted for by Eq. (26), is the plateau observed at higher temperatures, $T > 0.05 \text{ eV}$, where Z_{eff} goes well above the $1/\sqrt{T}$ curve. To find its possible origins let us first take a closer look at Eq. (26) and its predecessor, Eq. (19). For small impact positron energies ε the vibrational

excitation energy is given by $E_v \approx \varepsilon_A$. Accordingly, the resonance density $\rho(E_v)$ in Eq. (19) and the mean spacing D in Eq. (26) are approximately constant. As the positron energy, or temperature, increases, the resonance density factor should also increase, since $\rho(E_v)$ is a strong function of the excitation energy for multimode vibrational spectra. Therefore, the decrease of $Z_{\text{eff}}^{(\text{res})}$ should be slower than $1/k$, or $1/\sqrt{T}$. Moreover, the density factor may even produce a rise in the energy dependence of $Z_{\text{eff}}^{(\text{res})}$. In addition, contributions of higher positron partial waves which emerge as T, T^2 , etc., at small T , may also contribute to $Z_{\text{eff}}^{(\text{res})}$ in the plateau region. It might even seem that these effects could lead to a rapid increase of $Z_{\text{eff}}^{(\text{res})}$ with positron energy.

However, there is an effect that suppresses the increase of resonant annihilation. Throughout the paper I have assumed that the positron-molecule resonances have only two decay channels, annihilation and detachment, the latter being the reverse of positron capture. When the positron energy rises above the threshold of molecular vibrational excitations, the resonances can also decay into the ‘‘positron plus vibrationally excited molecule’’ channels. In this situation the total width of a resonance will be given by $\Gamma_v = \Gamma_a + \Gamma_c + \Gamma_v'$, where Γ_v' is the decay width due to positron detachment accompanied by the vibrational excitation of the molecule. This leads to a modification of Eq. (19), which now reads

$$Z_{\text{eff}}^{(\text{eff})} = \frac{2\pi^2 \rho_{ep}}{k} \rho(E_v) \left\langle \frac{\Gamma_c}{\Gamma_c + \Gamma_v'} \right\rangle. \quad (28)$$

This equation shows that as soon as the positron energy exceeds another inelastic vibrational-excitation threshold, the factor in brackets drops, thereby reducing the resonant annihilation contribution. Such downward steplike structures at vibrational thresholds are well known in dissociative electron attachment experiments (see, e.g., Refs. [30,42]). When the positron energy is well above the lowest inelastic vibrational threshold the ‘‘elastic’’ width Γ_c will become much smaller than the ‘‘inelastic’’ width Γ_v' , due to a large number of open inelastic vibrational-excitation scattering channels, and due to a kinematic increase of Γ_v' above the respective thresholds. This will strongly suppress the resonant annihilation contribution (28) with respect to that of Eq. (19) at larger positron energies. One may speculate that it is precisely the increase of Γ_v' that counteracts the rise of $\rho(E_v)$, and prevents rapid growth of $Z_{\text{eff}}^{(\text{eff})}$ with positron energies. It may also be true that a similar mechanism is behind the dramatic drop of the dissociative attachment cross sections for projectile energies above a few lower vibrationally inelastic thresholds [21,30].

IV. SUMMARY AND OUTLOOK

In this work I have considered two possible mechanisms of low-energy positron annihilation in binary collisions with molecules. The first mechanism is direct annihilation. It describes positron annihilation with atoms and small molecules, as well as molecules which do not form bound states

with the positron. The annihilation rate due to this mechanism has been related to the positron elastic scattering properties. In particular, it is enhanced when the positron has a low-lying virtual s -type level or a weakly bound state at $\varepsilon_0 = \pm \kappa^2/2$. For zero-energy positrons the direct annihilation rate is inversely proportional to $|\varepsilon_0|$. Small κ 's, together with the dipole polarizability of the target, also determine the rapid energy dependence of Z_{eff} at small positron energies. Estimates show that for room-temperature positrons Z_{eff} 's of up to 10^3 can be produced due the virtual or weakly bound state enhancement.

The second mechanism is resonant annihilation. It is operational when the positron forms temporary bound states with the molecule. As a necessary condition, the positron affinity of the molecule must be positive. The positron capture is a resonant process whereby the energy of the positron is transferred into vibrational excitations of the positron-molecule complex. The contribution of this mechanism to the annihilation rate is proportional to the level density of the positron-molecule resonances ρ . These resonances are characterized by the capture width Γ_c and annihilation width $\Gamma_a \sim 1 \mu\text{eV}$. For $\Gamma_c > \Gamma_a$ its contribution is independent of Γ_c , and is basically determined by the density ρ . The resonant mechanism can give very large annihilation rates (up to 10^8). Through its dependence on the vibrational excitation spectrum of the positron-molecule complex, this mechanism shows a high sensitivity to the chemical composition of the target and the size of the molecule. Both are essential features of the experimental data [4].

The difference between the two mechanisms is illustrated most clearly by comparison of the annihilation rates of alkanes and perfluoroalkanes. For example, C_6H_{14} has $Z_{\text{eff}} = 120\,000$, whereas for C_6F_{14} , Z_{eff} is only 630. The present theory attributes this huge difference to the fact that perfluorocarbons do not form bound states with the positrons, and, hence, the resonant annihilation is switched off for them. On the other hand, this mechanism is behind the high values of Z_{eff} for alkanes.

The experimental group at San Diego performed a number of measurements on protonated and deuterated molecules to test the sensitivity of Z_{eff} to the molecular vibrational modes [4,7]. For example, their data for benzene showed that

a replacement of a single hydrogen atom with deuterium changes the annihilation rate from $Z_{\text{eff}} = 15\,000$ for C_6H_6 to $Z_{\text{eff}} = 36\,900$ for $\text{C}_6\text{H}_5\text{D}$. On the other hand, the data on fully protonated vs fully deuterated alkanes show very little difference between the two cases. Such behavior is natural for smaller alkanes, e.g., methane, where direct annihilation is the dominant mechanism. However, observed for large alkanes, it cannot be readily interpreted by means of Eq. (19) or similar equations. It is possible that the vibrational excitations are dominated by low-lying C-C modes which are weakly affected by deuteration. On the other hand, deuteration may also influence positron coupling to the molecular vibrations, which will most likely lead to a reduction of Γ_c in Eq. (15). If the system is in the regime where $\Gamma_c \sim \Gamma_a$, this effect may offset the decrease of the vibrational spacings.

In spite of these difficulties, which could only be resolved by performing calculations for specific molecules, the present theory offers a consistent description of positron-molecule annihilation in real terms, through some well-defined parameters which characterize the system. It clearly identifies the two basic mechanisms of positron annihilation, and discusses their specific features. It also shows that studies of positron annihilation on molecules may give a unique insight into the physics of molecular reactions which go through the formation of vibrationally excited intermediate states. Such processes are very likely to be responsible for large dissociative electron attachment cross sections observed for molecules such as SF_6 . They are also of key importance for the whole class of chemical reactions, that is, for unimolecular reactions (see, e.g., Ref. [43]).

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