THEORY OF POSITRON ANNIHILATION ON MOLECULES

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Abstract Two basic mechanisms of positron annihilation in binary collisions with molecules are considered – direct and resonant. The contribution of the former is enhanced, together with the elastic scattering cross section, if the positron has a low-lying virtual level or a weakly bound state with the molecule. For room-temperature positrons it can give $Z_{\rm eff}$ up to 10^3. The latter mechanism is a two-stage process, whereby the positron is first captured into a vibrationally excited state of the positron-molecule complex, and then annihilates from this quasibound state. It operates only for molecules with positive positron affinities. Its contribution is proportional to the level density of the vibrational resonances, and may give $Z_{\rm eff}$ up to 10^8.

1. ANNIHILATION CROSS SECTIONS AND RATES

The process of electron-positron annihilation is described by quantum electrodynamics. In the non-relativistic Born approximation the annihilation cross section averaged over the electron and positron spins is given by [1]

$$\overline{\sigma}_{2\gamma} = \pi r_0^2 \frac{c}{v}, \qquad (1)$$

where v is the relative velocity, c is the speed of light, and r_0 is the classical electron radius defined by $e^2/r_0 = mc^2$, e and m being the electron charge and mass. The cross section (1) obeys a pure $1/v$-law, which characterises the near-threshold behaviour of inelastic processes with fast particles in the final state. Note that "near-threshold" here means $E \ll mc^2$, which is always true in the non-relativistic limit.

For small velocities $v \lesssim e^2/\hbar = 1$ au[1], the Born approximation is invalid, and it is necessary to take into account the electron-positron Coulomb interaction. The typical electron momenta in the annihilation process are $p \sim mc$. The corresponding distances $r \sim \hbar/mc$ are much smaller than those where the relative wavefunction ψ varies considerably, $r \sim a_0$. Therefore, in the non-relativistic limit the annihilation takes place when the electron and positron are found at the same point, and the cross section (1) must be multiplied by the density at the origin [2]

$$|\psi(0)|^2 = \frac{2\pi}{v(1 - e^{-2\pi/v})}, \tag{2}$$

where ψ is normalised to a plane wave $\psi(\mathbf{r}) \sim e^{i\mathbf{k}\cdot\mathbf{r}}$ at large distances. Obviously, this leads to an increase of the annihilation cross section.

When positrons annihilate on many-electron targets, such as atoms or molecules, the annihilation cross section is traditionally written as [3]

$$\sigma_a = \overline{\sigma}_{2\gamma} Z_{\text{eff}} = \pi r_0^2 \frac{c}{v} Z_{\text{eff}}, \tag{3}$$

The dimensionless *effective number of electrons* Z_{eff} allows for the fact that the target contains more than one electron, and takes into account the distortion of the positron wavefunction by the interaction with the target electrons. If the Born approximation were applicable at large positron velocities, Z_{eff} would be equal to the total number of electrons in the target Z.[2]

At small positron energies Z_{eff} can be very different from Z. First, there is a strong repulsion between the positron and the nucleus, which prevents the positron from penetrating deep into the atom. As a result, most of the annihilation events involve electrons of the valence and near-valence subshells, making Z_{eff} smaller. On the other hand, outside the target the positron motion is affected by an attractive *long-range* polarisation potential $-\alpha_d/2r^4$, where α_d is the dipole polarisability of the target. This leads to an increase of the positron density near the target and enhances Z_{eff}. There is also a *short-range* enhancement of Z_{eff} due to the Coulomb interaction which draws together the annihilating

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[1] Atomic units $m = |e| = \hbar$, where $c = \alpha^{-1} \approx 137$ and the Bohr radius $a_0 = \hbar^2/me^2 = 1$, are used throughout the paper.

[2] Of course, at large velocities one must also consider other inelastic processes such as positronium (Ps) formation which leads to positron annihilation. In fact Eq. (3) only makes sense for targets with ionisation potentials I above the Ps ground-state binding energy $|E_{1s}| = 6.8$ eV. For targets with $I < 6.8$ eV, the inelastic Ps-formation channel is open right from threshold, and Ps formation followed by its annihilation is the dominant annihilation mechanism. The latter is also true for targets with $I > |E_{1s}|$ at positron energies $\varepsilon > I - |E_{1s}|$.

electron and the positron. It has the same physical origin as Eq. (2), although this equation is not directly applicable. For bound electrons there is a whole distribution of relative velocities $v \sim 1$ au, and the electron-positron Coulomb attraction is screened when the positron is outside the target. This short-range effect should be stronger for targets with loosely bound electrons which have smaller momenta.

Mathematically all these effects are described by a formula which follows from the definition (3) and discussion above Eq. (2):

$$Z_{\rm eff}(k) = \int \sum_{i=1}^{Z} \delta(\mathbf{r}-\mathbf{r}_i)|\Psi_{\mathbf{k}}(\mathbf{r}_1,\dots,\mathbf{r}_Z,\mathbf{r})|^2 d\mathbf{r}_1\dots d\mathbf{r}_Z d\mathbf{r}\ , \qquad (4)$$

where $\mathbf{r}_i$ 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 wavefunction 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 normalised at large distances as

$$\Psi_{\mathbf{k}}(\mathbf{r}_1,\dots,\mathbf{r}_Z,\mathbf{r}) \simeq \Phi_0(\mathbf{r}_1,\dots,\mathbf{r}_Z)e^{i\mathbf{k}\mathbf{r}}. \qquad (5)$$

Equation (4) refers to annihilation in binary positron-molecule collisions. This regime is realised in experiments performed at low gas densities n, and the quantity measured is the annihilation rate

$$\lambda = \sigma_a v n = \pi r_0^2 c Z_{\rm eff} n. \qquad (6)$$

In experiments the positrons are usually not monoenergetic, but rather characterised by a momentum distribution. For thermalised positrons the latter is Maxwellian, and the experimental value of $Z_{\rm eff}$ corresponds to a Maxwellian average of $Z_{\rm eff}(k)$. Equation (6) is also used to describe experiments at large densities where $Z_{\rm eff}$ becomes density dependent [4].

2. $Z_{\rm eff}$ FOR ATOMS AND MOLECULES

The most accurate $Z_{\rm eff}$ values have been obtained in calculations for simple systems like H and He [5, 6], and in experiments for He [7]. For other systems experimental values are more reliable, although there is a good theoretical understanding of $Z_{\rm eff}$ for noble-gas atoms [8, 9], and there have been several calculations for simple molecules [10, 11, 12].

A collection of $Z_{\rm eff}$ for the hydrogen and noble-gas atoms, simple inorganic molecules and alkanes and their perhalogenated substitutes is presented in Tables 1, 2 and 3. Earlier experimental data were obtained by observing annihilation of positrons from a radioactive source in dense gases. However, most of the information on Z_{eff}, especially for large organic molecules, comes from measurements in a positron trap [13, 14]. This set-up ensures that the positrons are fully thermalised, and the annihilation takes place in binary collisions, since the tested species are introduced at very low pressures.

Table 1. Hydrogen and noble gases.

Atom	Z_{eff}	Comment
H	8^a	Calc.
He	3.94^b	Exp.
Ne	5.99^b	Exp.
Ar	26.7^b, 33.8^c	Exp.
Kr	65.7^d, 90.1^c	Exp.
Xe	320^d, 401^c	Exp.

[a] At thermal $k = 0.05$, Ref. [5].
[b] Measured in a gas [7].
[c] Measured in the positron trap [14].
[d] Measured in a gas [15].

Table 2. Simple molecules.

Molecule	Z_{eff}	Dipole moment (Debye)
H_2	14.6^a	–
N_2	30.5^b	–
O_2	36.7^c	–
CO	38.5^b	0.112
CO_2	54.7^d	–
N_2O	78^b	0.17
SF_6	86.2^c	–
H_2O	319^c	1.85
NO_2	1090^b	0.32
NH_3	1600^b	1.47

[a] Ref. [16], [b] Ref. [17], [c] Ref. [14], [d] Ref. [15]

It is obvious from Table 1 that even for atoms Z_{eff} considerably exceeds the number of the valence electrons. A simple possibility for enhanced annihilation was pointed out in [18]. It is realised when the positron forms a low-lying virtual level or a weakly bound state with the target, at the energy $\varepsilon_0 = \pm\kappa^2/2$. In both cases $Z_{\mathrm{eff}} \propto 1/|\varepsilon_0|$, and the magnitude of low-energy elastic scattering cross section is similarly enhanced: $\sigma_{\mathrm{el}} \simeq 4\pi/\kappa^2$ (see Sec. 3). The noble-gas atom sequence illustrates this effect nicely. The increase of the dipole polarisability and the decrease of the ionisation potential leads to stronger positron-atom attraction, lowering of the virtual states (smaller κ), and rapid growth of Z_{eff} [9, 19].

However, this type of enhancement is limited by finite positron momenta, as the growth of both σ_{el} and Z_{eff} saturates for $\kappa < k$ [20]. For room-temperature positrons $k \sim 0.05$ au, values of Z_{eff} much greater than that of Xe ($|\kappa| \sim 10^2$) cannot be obtained.

Turning to molecules now, we see that enhanced direct annihilation may account for Z_{eff} for most simple inorganic molecules, as well as CH_4, C_2H_6 and fluoroalkanes, Tables 2 and 3. However, Z_{eff} for NO_2 and NH_3 are already at its limit, and those of heavier alkanes and chloro- and bromoalkanes are way beyond it. The record Z_{eff} values found are

Table 3. Alkanes and perhalogenated alkanes C_nX_{2n+2}.

	$Z_{\rm eff}$			
Molecule	X = H	X = F	X = Cl	X = Br
CX_4	142[a]	54.4	9 530	39 800
C_2X_6	660[b]	152	68 600	–
C_3X_8	3 500[b]	317	–	–
C_4X_{10}	11 300	–	–	–
C_5X_{12}	37 800	–	–	–
C_6X_{14}	120 000	630	–	–
C_7X_{16}	242 000	–	–	–
C_8X_{18}	585 000	1 064	–	–
C_9X_{20}	643 000	–	–	–
$C_{10}X_{22}$	728 000	–	–	–
$C_{12}X_{26}$	1 780 000	–	–	–
$C_{16}X_{34}$	2 230 000	–	–	–

[a] Ref. [15], [b] Ref. [17]; the rest are measurements in the positron trap [14].

4.3×10^6 for antracene $C_{14}H_{10}$ [21] and 7.5×10^6 for sebacic acid dimethyl ester $C_{12}H_{22}O_4$ [22]. In fact, the first observations of high annihilation rates for alkanes with $n = 1$–4 and CCl_4 were made in 1960's [23].

What makes the $Z_{\rm eff}$ data remarkable is not just their magnitude, but the very rapid dependence on the size of the molecule, e.g. $Z_{\rm eff} \propto N^6$ for alkanes, where N is the number of atoms. There is also a striking contrast between the alkanes and their fluorinated counterparts. In spite of a much greater number of valence electrons in the latter, their $Z_{\rm eff}$ increase almost linearly with the size of the molecule. This is an example of a strong chemical sensitivity illustrated further in Table 4, which shows that replacing one hydrogen atom by another atom or a small group leads to huge changes in $Z_{\rm eff}$. As a result of high annihilation rates, many large organic molecules display large ionization-fragmentation cross sections by positrons at sub-Ps-threshold energies [24]. Clearly, these phenomena cannot be explained by a simple picture of *direct* "in-flight" annihilation of the positron.

Table 4. Benzene and substituted benzenes.

Molecule	C_6H_6	C_6H_5D	C_6H_5F	C_6H_5Cl	C_6H_5Br	$C_6H_5(CH_3)$	$C_6H_5(NO_2)$
$Z_{\rm eff}$[a]	15 000	36 900	34 000	72 300	172 000	190 000	430 000

[a] Experimental data from Ref. [14].

The estimates of $Z_{\rm eff}$ made above ignore the possibility of positron capture by an atom or molecule, which would be possible if the positron had a bound state with the target. In fact, high $Z_{\rm eff}$ values have always been interpreted as an indirect evidence of the existence of such states [13, 17, 23].

The only way for a free positron to shed excess energy and become truly bound in a binary collision is via radiative recombination. The corresponding rate $\lambda_{\rm rad} \propto c^{-3}$ [25], has the same magnitude in powers of c as direct annihilation (6), and its contribution to annihilation is small, $\Delta Z_{\rm eff} \lesssim 1$.

For a positron colliding with a molecule the energy can be absorbed by molecular vibrations[3]. Since the spectrum of molecular vibrations is discrete, this may only take place at specific positron energies $\varepsilon = E_v + \varepsilon_0$, where ε_0 is the energy of the positron-molecule bound state, and E_v is the energy of the vibrational excitation. These energies correspond to the positions of positron-molecule *resonances*, or quasi-bound states. The resonances have finite energy widths $\Gamma = \hbar/\tau$, where τ is their lifetimes. The latter are determined by the positron annihilation rate in the (quasi)bound state, as well as the rate of positron emission back into the continuum[4].

Such resonances, often called vibrational Feshbach resonances, are well known in electron-molecule scattering [27]. For positrons, the contribution of a single resonance to the annihilation rate was considered theoretically in [28, 29]. The resonances were also thought to be behind the large annihilation rates and strong dependence on the molecular size for alkanes [13], and in Ref. [30] they were mentioned in relation to the problem of fragmentation of molecules by positron annihilation. However, only in a recent paper [20] the contribution of resonant annihilation to $Z_{\rm eff}$ has been properly related to the widths and density of the resonances and their symmetry (see Sec. 4). Most importantly, the analysis shows that the resonant mechanism fully accounts for most of the observed effects.

A necessary condition for the resonant annihilation is the existence of the positron-molecule bound state. Untill recently very little was known

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[3] Electronic excitations have to be ruled out. For most of the molecules they lie above a few eV and are inaccessible for thermal positrons. On the other hand, molecular rotations have very small level spacings. However, at low energies the positron wavefunction is dominated by the s wave, and exchange of angular momentum between the positron and the molecule is suppressed, at least for non-polar molecules.

[4] If the quasibound positron-molecule complex undergoes collisions with other molecules, it can be stabilised against positron emission. This effect will result in density dependent $Z_{\rm eff}$ [26], and should not be considered in the binary-collision regime.

for certain about the possibility of positron binding to neutral atoms or molecules. This situation has changed dramatically now, at least in regards to positron-atom bound states [31, 32]. At present there are about ten atoms for which binding has been either proved or established beyond resonable doubt in theoretical calculations. This development was not entirely unexpected [33]. Even the information inferred from $Z_{\rm eff}$ about the virtual states for positrons on noble gas atoms suggests that neutral species with dipole polarisabilities greater, and ionization potentials smaller than those of Xe, are likely to form such bound states. However, obtaining accurate binding energies is a difficult problem [31]. It requires the use of sophisticated computational tools to account for strong electron-positron correlations.

Much less is known about positron binding with molecules. It has been demonstrated in calculations for a few strongly polar diatomic molecules [32], e.g. LiH, BeO and LiF. Unlike atoms, these molecules bind positrons even in the static Hartree-Fock approximation, although correlations are very important in determining the actual value of the binding energy [34, 35, 36, 37].

Annihilation data do not show much correlation between $Z_{\rm eff}$ and the size of the molecular dipole moments [14]. For non-polar molecules large $Z_{\rm eff}$ which cannot be accounted for by the direct annihilation mechanism, present the strongest evidence for the existence of positron-molecule bound states and vibrational resonances (Sec. 4).

3. DIRECT ANNIHILATION

Let us first assume that the electron-positron degrees of freedom are completely decoupled from the nuclear motion, e.g. if the nuclei are fixed at their equilibrium positions. The scattering wavefunction is then determined by the positron interaction with the charge distribution of the ground-state target and electron-positron correlation interaction (polarisation of the target, virtual Ps formation, etc.). The corresponding wavefunction $\Psi_{\mathbf{k}}$ satifies the Schrodinger equation

$$(T + U - E_0)\Psi_{\mathbf{k}} = \varepsilon\Psi_{\mathbf{k}}, \tag{7}$$

where T is the kinetic energy operator, U is the sum of all Coulomb interactions between the particles, E_0 is the target ground-state energy and $\varepsilon = k^2/2$ is the positron energy.

Consider annihilation at positron energies well below the Ps-formation threshold. Although the positron pulls the target electrons towards it[5],

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[5] A simple way to estimate this effect is to consider the formation of virtual Ps. The energy of its centre-of-mass motion is negative, $\varepsilon - I - E_{1s} \equiv E_{\rm Ps} < 0$, and the Ps atom cannot

the annihilation takes place within the range of the ground-state electron cloud [38]. In other words, the positron annihilates when it is at the target, and the distances which contribute to the $Z_{\rm eff}$ integral (4) are small. At such distances the interaction between the particles, represented by U on the left-hand side of (7), is much greater than the positron energy. Therefore, the $\varepsilon\Psi_{\mathbf{k}}$ term can be neglected and the solution of the equation $\Psi_{\mathbf{k}}$ at small distances *does not depend on the positron energy*, except through a normalisation factor.

In accord with Eq. (5), the wavefunction Ψ_k when the positron is just outside the target contains a linear combination of the incident and scattered positron waves

$$\Psi_{\mathbf{k}}(\mathbf{r}_1,\ldots,\mathbf{r}_Z,\mathbf{r}) = \Phi_0(\mathbf{r}_1,\ldots,\mathbf{r}_Z)\left[e^{i\mathbf{kr}} + f_{\mathbf{kk}'}\frac{e^{ikr}}{r}\right] , \qquad (8)$$

where $f_{\mathbf{kk}'}$ is the scattering amplitude. Taken at the target boundary $r = R$, this function determines the normalisation of $\Psi_{\mathbf{k}}$ inside the target, where the annihilation takes place. For low positron momenta $kR \ll 1$, the scattering is dominated by the s wave and $f_{\mathbf{kk}'}$ can be replaced by the s-wave amplitude f_0. As a result, the integrand in $Z_{\rm eff}$ of Eq. (4) is proportional to

$$\left|1+\frac{f_0}{R}\right|^2 , \qquad (9)$$

and one obtains the following estimate [20]

$$Z_{\rm eff}^{(\rm dir)} \simeq 4\pi\rho_e\delta R\left(R^2 + 2R{\rm Re}f_0 + \frac{\sigma_{\rm el}}{4\pi}\right) , \qquad (10)$$

where ρ_e is the electron density in the annihilation range (possibly be enhanced due to short-range electron-positron correlations), δR is the range of distances where the positron annihilates, and $\sigma_{\rm el}$ is the elastic cross section, which is dominated by the s-wave contribution, $\sigma_{\rm el} \simeq \sigma_0 = 4\pi|f_0|^2$, at low positron momenta [42]. In the zero-energy limit it is determined by the scattering length a, $\sigma_{\rm el} = 4\pi a^2$, since $f_0 = -a$ for $k = 0$. Note that if the target has a permanent dipole moment, the long-range $1/r^2$ dipole potential dominates the low-energy scattering and makes the derivation of Eq. (10) invalid. In particular, it makes $\sigma_{\rm el}$ infinite [2], while $Z_{\rm eff}$ remains finite.

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move far away from the parent target. Its wavefunction behaves as $\exp[-(4|E_{\rm Ps}|)^{1/2}R]$, and $R_{\rm Ps} \sim (4|E_{\rm Ps}|)^{-1/2}$ estimates how far the virtual Ps can be from the target. For small ε this distance remains small, e.g. for $I = 10$ eV, $R_{\rm Ps} \sim 1.5$ au.

Equation (10) allows one to analyse the typical features of $Z_{\rm eff}$ due to direct annihilation. The factor $4\pi\rho_e\delta R \equiv F$ in (10) can be estimated using the electron density at the origin of Ps(1s), $\rho_e \sim \rho_{\rm Ps} = 1/8\pi$, and $\delta R \sim 1$, which yields $F \sim 0.5$. Therefore, unless $\sigma_{\rm el}$ is much greater than the geometrical size of the target, direct annihilation gives $Z_{\rm eff} \sim 1$–10.

When the scattering cross section is large the annihilation rate is greatly enhanced. Indeed, if the positron has a virtual or bound state with the energy close to zero, $\varepsilon_0 = \pm\kappa^2/2$, $|\kappa| \ll R^{-1}$, the s-wave scattering amplitude is given by [2]

$$f_0 = -\frac{1}{\kappa + ik}, \qquad (11)$$

and the cross section peaks strongly at small momenta, $\sigma_{\rm el} \simeq 4\pi/(\kappa^2 + k^2)$, its magnitude being much greater than the geometrical size of the target[6]. In this case the last term in brackets in Eq. (10) dominates, and $Z_{\rm eff}^{\rm (dir)}$ shows a similar peak [18, 19, 43],

$$Z_{\rm eff}^{\rm (dir)} \simeq F\frac{1}{\kappa^2 + k^2}. \qquad (12)$$

At zero positron energy both $\sigma_{\rm el}$ and $Z_{\rm eff}^{\rm (dir)}$ can be made arbitrarily large by choosing ever smaller κ. However, for finite momenta the maximal possible values of $Z_{\rm eff}^{\rm (dir)}$ are limited, e.g. for room temperature positrons, $k \sim 0.05$,

$$Z_{\rm eff}^{\rm (dir)} \lesssim 10^3. \qquad (13)$$

This means that relatively large values of $Z_{\rm eff}$ can still be understood in terms of the direct annihilation mechanism enhanced by the presence of a low-lying virtual or weakly-bound positron-target state. On the other hand, observations of $Z_{\rm eff} > 10^3$ with room-temperature positrons most certainly require a different mechanism.

Figure 1 illustrates a strong correlation between the elastic scattering and $Z_{\rm eff}^{\rm (dir)}$ suggested by Eq. (10). It presents a selection of $Z_{\rm eff}$ values for a number atoms and small molecules, as a function of $\sigma_{\rm el}$. For atoms the data are taken from the theoretical calculations of Ref. [44] for hydrogen, and Ref. [8] for He, Ne, Ar, Kr and Xe. Since Eq. (10) is valid for low positron momenta, only a few data points with $k \leq 0.2$ are used for each atom. Plotted for molecules are the experimental $Z_{\rm eff}$ from

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[6] It must be mentioned that the long-range $-\alpha_d/2r^4$ polarisation potential modifies this functional form, and in particular leads to a more rapid k-dependence of $\sigma_{\rm el}$ and $Z_{\rm eff}^{\rm (dir)}$, see Ref. [20], Eqs. (22) and (23). However, this does not affect the present estimates of $Z_{\rm eff}^{\rm (dir)}$.

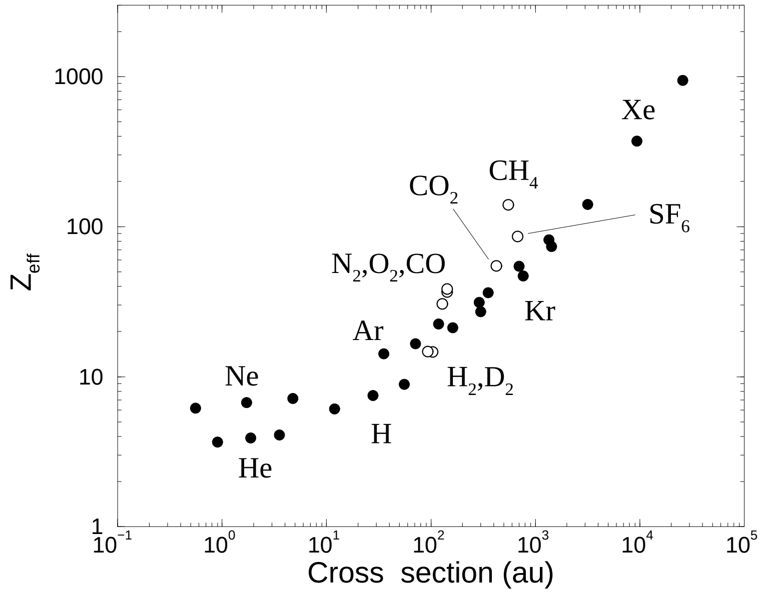

Figure 1. Relation between the elastic scattering cross section $\sigma_{\rm el}$ and $Z_{\rm eff}$ for atoms (●) and simple molecules (○). A strong correlation between the two expressed by Eq. (10) is characteristic of the direct annihilation mechanism.

Refs. [14, 17], against the momentum-transfer cross sections σ_m from Ref. [45], obtained with room-temperature positrons[7]. As seen from the figure, within a factor of 2 or 3, the relation between $Z_{\rm eff}$ and $\sigma_{\rm el}$ holds over a very large range of their values.

In the case when the positron forms a weakly bound state with the atomic system (with $I > 6.8$ eV), one can also relate $Z_{\rm eff}$ at zero energy to the spin-averaged positron annihilation rate in the bound state [46]. Neglecting 3γ annihilation, the latter is given by

$$\Gamma_a = \pi r_0^2 c \int \sum_{i=1}^{Z} \delta(\mathbf{r}-\mathbf{r}_i)|\Psi_0(\mathbf{r}_1,\dots,\mathbf{r}_Z,\mathbf{r})|^2 d\mathbf{r}_1 \dots d\mathbf{r}_Z d\mathbf{r} \ , \qquad (14)$$

where Ψ_0 is the wavefunction of the bound state. When the positron is outside the atomic system, i.e. at $r > R$, we have

$$\Psi_0(\mathbf{r}_1,\dots,\mathbf{r}_Z,\mathbf{r}) \simeq \Phi_0(\mathbf{r}_1,\dots,\mathbf{r}_Z)\frac{A}{r}e^{-\kappa r}, \qquad (15)$$

where A is the asymptotic normalisation constant. For a weakly bound state ($\kappa \ll R^{-1}$) the positron exponent in (15) is very diffuse. The main

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[7] At low projectile energies s-wave scattering dominates and $\sigma_{\rm el} \approx \sigma_m$.

contribution to the normalisation integral

$$\int |\Psi_0(\mathbf{r}_1, \ldots, \mathbf{r}_Z, \mathbf{r})|^2 d\mathbf{r}_1 \ldots d\mathbf{r}_Z d\mathbf{r} = 1, \tag{16}$$

comes from large positron distances, and after substituting (15) we obtain $A = \sqrt{\kappa/2\pi}$. At zero positron energy we can use the amplitude $f_0 = -1/\kappa$ in Eq. (8), and neglect the incident plane wave in comparison with f_0/r, since f_0 is anomalously large. In this case a comparison of Eqs. (4) and (8) with (14) and (15), immediately yields

$$Z_{\text{eff}}(0) = \frac{\Gamma_a}{\pi r_0^2 c} \left| \frac{f_0}{A} \right|^2 = \frac{\Gamma_a}{\pi r_0^2 c} \frac{2\pi}{\kappa^3}. \tag{17}$$

In Table 5 we have applied this formula to estimate $Z_{\text{eff}}(0)$ for a number of atoms and LiH molecule where bound positron states were obtained in large-scale stochastic variational calculations [31]. It is obvious that larger Z_{eff} are found for those atoms which have smaller κ, i.e. where the enhancement due to a weakly-bound state is stronger.

Table 5. Estimates of Z_{eff} for atomic systems which form bound states with positrons.

Atom or molecule	$\lvert\varepsilon_0\rvert^a$ (au)	$\Gamma_a{}^a$ (10^9 s^{-1})	κ^b	$Z_{\text{eff}}{}^c$
Be	0.002775	0.397	0.0745	120
Mg	0.013906	0.838	0.1668	22.5
Zn	0.001425	0.248	0.0534	203
Cu	0.005518	0.576	0.1051	62
Ag	0.005512	0.598	0.1050	64
LiH	0.033418	1.643	0.2585	12^d

[a] Binding energies and spin-averaged annihilation rates from Ref. [37, 47].
[b] Calculated values $\kappa = (2|\varepsilon_0|)^{1/2}$.
[c] Estimates of Z_{eff} at zero positron energy, Eq. (17). The latter is written in atomic units, and a simple conversion formula can be used: $(10^9\ \text{s}^{-1})/(\pi r_0^2 c) = 0.0198$ au.
[d] For LiH this value is the contribution of direct annihilation alone (see end of Sec. 3). Note also that LiH is a strongly polar molecule, which may affect the validity of Eq. (17).

Let us now follow the same line of argument which lead from Eq. (4) via Eq. (8) to the estimate of $Z_{\text{eff}}^{(\text{dir})}$ by Eq. (10). Starting from Γ_a (14) and using Eq. (15) we obtain

$$\Gamma_a \simeq \pi r_0^2 c \, 4\pi \rho_e \delta R |A|^2 = \pi r_0^2 c \, 4\pi \rho_e \delta R \, \frac{\kappa}{2\pi}. \tag{18}$$

This formula shows that Γ_a is proportional to κ, i.e. positron states with smaller binding energies have lower annihilation rates. This is a simple manifestation of the normalisation of the positron wavefunction. A smaller κ corresponds to a more diffuse positron cloud, hence, a smaller probability to find the positron in the vicinity of the atom, where the annihilation takes place. This result is also discussed in Ref. [43].

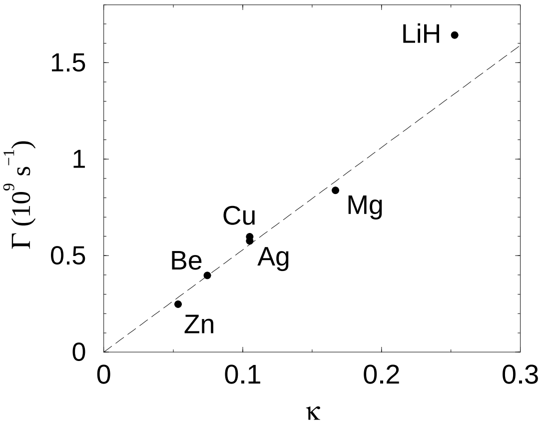

Figure 2. Dependence of the annihilation rate of positronic compounds on the bound-state parameter κ. The dashed line is a fit $\Gamma_a = 5.3\kappa\ 10^9\ \mathrm{s}^{-1}$.

The plot of Γ_a vs κ based on the data from Table 5 supports the validity of Eq. (18). Even the datum for the LiH molecule, in spite of its large dipole moment (5.884 Debye [48]) and relatively large κ, follows the trend. The slope of the straight-line fit can be used to estimate the factor $F = 4\pi\rho_e\delta R$. This gives $F \approx 0.66$, remarkably close to our earlier crude estimate.

The value of Z_{eff} for LiH given in Table 5 represents only the contribution of direct annihilation. For this molecule the positron binding energy $|\varepsilon_0| = 0.909$ eV is greater than its vibrational frequency $\omega = 0.1743$ eV [49]. As a result, the e^+LiH compound should possess a series of vibrationally excited bound states [50]. Such states could manifest as resonances in the positron-molecule continuum[8], and give an additional contribution to Z_{eff}. Let us analyse this possibility in detail.

4. RESONANT ANNIHILATION

The annihilation mechanism discussed in this section operates for molecules which have bound states with the positron. Assuming that the coupling V between the electron-positron and nuclear degrees of

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[8] For positrons scattered from LiH the lowest inelastic threshold open at all positron positron energies, is dissociation into Li^+ and PsH. Formation of PsH followed by positron annihilation within it will probably be the main annihilation channel for this particular molecule.

freedom is small, we can represent the total scattering wavefunction for such targets as

$$|\Psi_{\mathbf{k}}\rangle + \sum_{\nu} \frac{|\Psi_\nu\rangle\langle\Psi_\nu|V|\Psi_{\mathbf{k}}\rangle}{E - E_\nu + \frac{i}{2}\Gamma_\nu} \ . \tag{19}$$

Here $\Psi_{\mathbf{k}}$ describes direct, or *potential* [2] scattering of the positron by the ground-state molecule, which we examined in Sec. 3. The second term has the appearance of a standard perturbation-theory formula. It describes positron capture into vibrationally excited (quasibound) states Ψ_ν of the positron-molecule compound[9]. Their energies are complex, $E_\nu - \frac{i}{2}\Gamma_\nu$, because these states are unstable against positron annihilation and positron re-emission back into the continuum. The width Γ_ν is the sum of the annihilation and emission widths: $\Gamma_\nu = \Gamma_a^\nu + \Gamma_e^\nu$. This formula implies that at low positron energies the only open inelastic channel is annihilation. For positron energies above the molecular excitation threshold the width will also contain a contribution from positron emission accompanied by excitation of the target.

The capture into the state ν is maximal when the energy of the system $E = E_0 + \varepsilon$ (E_0 is the target ground-state energy) is close to E_ν, i.e. the resonances are observed at positron energies $\varepsilon_\nu = E_\nu - E_0$. The contribution of a resonance ν to the annihilation cross section is given by the standard Breit-Wigner formula [2]:

$$\sigma_a^{(\nu)} = \frac{\pi}{k^2} \frac{\Gamma_a^\nu \Gamma_e^\nu}{(\varepsilon - \varepsilon_\nu)^2 + \frac{1}{4}\Gamma_\nu^2}, \tag{20}$$

where we assume that the positron is in the s wave[10]. In terms of Z_{eff} defined by Eq. (3), this means

$$Z_{\text{eff}}^{(\nu)} = \frac{\pi}{k} \frac{\Gamma_a^\nu}{\pi r_0^2 c} \frac{\Gamma_e^\nu}{(\varepsilon - \varepsilon_\nu)^2 + \frac{1}{4}\Gamma_\nu^2}. \tag{21}$$

The annihilation width Γ_a^ν is given by a formula similar to Eq. (14), and the ratio $\Gamma_a^\nu/\pi r_0^2 c$ is the average electron density at the positron ρ_{ep}. The index ν has been dropped because this density is practically the same for different nuclear vibrational states (as is Γ_a^ν). A simple estimate of ρ_{ep} is provided by Eq. (18),

$$\rho_{ep} \simeq 4\pi\rho_e \delta R \frac{\kappa}{2\pi} \equiv F \frac{\kappa}{2\pi}. \tag{22}$$

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[9] In the first approximation they can be written as $\Psi_\nu = \Psi_0\psi_\nu$, where Ψ_0 is the electron-positron bound state wavefunction, and ϕ_ν are the wavefunctions of the nuclear motion.

[10] Contributions of the higher partial waves contain an additional factor $2l + 1$.

Using $F = 0.66$ obtained from Figure 2 we find that for a state bound by 1 eV ($\kappa = 0.27$) this density is about 70% that of Ps, $\rho_{\rm Ps} = (8\pi)^{-1}$, and $\rho_{ep} \sim \rho_{\rm Ps}$ can be used for rough estimates. This corresponds to the annihilation width $\Gamma_a = \pi r_0^2 c/8\pi = 5 \times 10^{-8}$ au ~ 1 μeV.

The spectrum of vibrational excitations in large molecules can be very dense. Hence, contributions of many resonances must be included:

$$Z_{\rm eff}^{(\rm res)} = \frac{\pi}{k}\rho_{ep}\sum_{\nu}\frac{\Gamma_e^{\nu}}{(\varepsilon-\varepsilon_{\nu})^2+\frac{1}{4}\Gamma_{\nu}^2}. \tag{23}$$

For non-monochromatic positrons the individual resonances cannot be resolved, and the observed rate corresponds to an average

$$\frac{1}{\Delta}\int Z_{\rm eff}^{(\rm res)} d\varepsilon \tag{24}$$

over an energy interval Δ which contains many resonances. The contribution of any given resonance drops rapidly for $|\varepsilon - \varepsilon_{\nu}| > \Gamma_{\nu}$, and the integration can be taken formally from $-\infty$ to $+\infty$. This gives

$$Z_{\rm eff}^{(\rm res)} = \frac{2\pi^2}{k}\frac{\rho_{ep}}{D}\left\langle\frac{\Gamma_e^{\nu}}{\Gamma_{\nu}}\right\rangle, \tag{25}$$

where D is the mean energy spacing between the resonances, and $\langle \dots \rangle$ denotes the average value[11].

At this point the origin and size of enhancement of $Z_{\rm eff}$ due to the positron-molecule resonances become clear [20]. If the positron emission width of the resonances is not too small, $\Gamma_e^{\nu} > \Gamma_a^{\nu} \sim 1$ μeV, we have $\Gamma_{\nu} = \Gamma_e^{\nu} + \Gamma_a^{\nu} \approx \Gamma_e^{\nu}$, and

$$Z_{\rm eff}^{(\rm res)} \simeq \frac{2\pi^2}{k}\frac{\rho_{ep}}{D}. \tag{26}$$

This result means that $Z_{\rm eff}^{(\rm res)}$ is simply proportional to the energy density of vibrational resonances D^{-1}. In heavier and larger molecules vibrational level spacings D become small, which means that very large $Z_{\rm eff}$ can be obtained.

Take for example a simple $\rm Cl_2$ molecule [51]. It has a single vibrational mode $\omega = 560$ cm$^{-1} = 2.55 \times 10^{-3}$ au [48]. Assuming that a weakly bound positron makes little change in the vibrational frequency, $D \approx \omega$,

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[11] A similar estimate of the resonant contribution to the elastic scattering, $\sigma_{\rm el}^{(\rm res)} = 2\pi^2/k^2\langle(\Gamma_e^{\nu})^2/D\Gamma_{\nu}\rangle$, shows that it is not enhanced compared with the potential scattering. On the contrary, it is probably quite small.

and using $\rho_{ep} = \rho_{\mathrm{Ps}}$, we obtain $Z_{\mathrm{eff}}^{(\mathrm{res})} = 6 \times 10^3$ at $k = 0.05$. This value is much greater than the maximal $Z_{\mathrm{eff}}^{(\mathrm{dir})}$. In fact, it is also greater than the experimental $Z_{\mathrm{eff}} = 1600$ [52]. This apparent discrepancy is easy to account for. Firstly, for a weakly bound state with a small κ, ρ_{ep} is smaller than ρ_{Ps}, see Eq. (22). Secondly, the vibrational spacing for Cl_2 is greater than the thermal energy $k_B T = 204$ cm^{-1} (at $T = 293$ K). Therefore, there is at most one resonance within the positron energy range and instead of using Eq. (26) a proper Maxwellian average should be taken (see below).

The vibrational spectrum density increases rapidly with the size of the molecule. This would explain the experimental results for alkanes, Table 3. Perfluorinated alkanes have smaller vibrational spacings. The only way to understand their small Z_{eff} is to conclude that resonant annihilation is simply switched off for them, because the positrons do not bind to these molecules[12], as well as to SF_6 [53]. Indeed, Z_{eff} for perfluoroalkanes are within reach of the direct mechanism, their increase with the size of the molecule caused by lowering of the virtual state. On the other hand, replacing hydrogen atoms with Cl or Br lowers the vibrational frequencies and retains (or even strengthens) the positron binding, and makes resonant annihilation stronger.

The maximal value of $Z_{\mathrm{eff}}^{(\mathrm{res})}$ is obtained for the smallest spacing $D \sim \Gamma_\nu$ when $\Gamma_e^\nu = \Gamma_a^\nu$. For room temperature positrons this means

$$Z_{\mathrm{eff}}^{(\mathrm{res})} < 5 \times 10^7, \tag{27}$$

which corresponds to the unitarity limit of the s-wave annihilation cross section: $\sigma_a \leq \pi/k^2$.

Equation (25) also shows that a common notion that larger resonance lifetimes $\tau_\nu = 1/\Gamma_\nu$ mean greater annihilation rates, is incorrect. This notion originates in a classical picture which tells that the probability of positron annihilation is proportional to the time it spends near the target. The classical picture itself is in fact correct, but one must remember that the classical period of motion corresponds to $\hbar/(E_{\nu+1} - E_\nu)$, where $E_{\nu+1} - E_\nu$ is the difference between two consecutive eigenstates [2]. This period appears in Eqs. (25) and (26) as the $1/D$ factor.

The lifetimes of the resonances are limited by annihilation: $\tau_\nu < 1/\Gamma_a^\nu$. Maximal lifetimes are achieved for $\Gamma_e^\nu \ll \Gamma_a^\nu$. However, very small emission widths mean that the resonances become almost decoupled from the positron-molecule continuum. In this case the resonant annihilation

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[12] Fluorine atoms, similarly to Ne, appear to be fairly "unattractive" to positrons [20, 41], because of their small α_d and large ionization potential.

falls below that of Eq. (26), because the positrons do not get into the resonant states.

The positron-molecule resonance density D^{-1} in Eqs. (25) and (26) depends on the excitation energy available, as defined by the positron kinetic energy and positron affinity, $\varepsilon+|\varepsilon_0|$, and also on the structure of the molecular vibrational spectrum. Suppose that the molecule possesses a particular symmetry. Its electronic ground-state wavefunction is usually nondegenerate 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 forms a bound state with the molecule, the electron-positron part of the wavefunction of the positron-molecule complex will also be fully symmetric, i.e., of the A symmetry type.

Consider now capture of a continuous spectrum positron into the bound positron-molecule state. At low energies the incident positron s wave dominates. As a result, the electron-positron part of the wavefunction of the initial (molecule and the 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 constraint on the nuclear vibrations excited during the capture process. They must also belong to the A symmetry type.

This selection rule limits the spectrum of possible vibrationally excited resonances. It allows arbitrary excitations and combinations of the A modes. It also allows overtones and combinations of 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 [2]. This does not mean that all such vibrations will contribute to the density factor D^{-1} in Eq. (26). Some of them may have extremely weak coupling to the electron-positron degrees of freedom ($\Gamma_e^\nu \ll 1\ \mu$eV). In this case they will be effectively decoupled from the positron capture channel, and hence, will not contribute to $Z_{\rm eff}$.

The role played by symmetry of the nuclear vibrational resonances results in a strong chemical sensitivity of $Z_{\rm eff}$. For example, replacing a single hydrogen atom in benzene by deuterium changes the molecular symmetry and increases the number of fully symmetric vibrational modes, which is matched by an increase of $Z_{\rm eff}$ in Table 3[13].

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[13] Experiments show that for methane and heavy alkanes full deuteration results in a relatively minor change of $Z_{\rm eff}$ [41], in spite of the obvious reduction of the vibrational frequencies. However, deuteration has a smaller effect on the low-frequency backbone C−C modes, which probably play the main part in positron capture.

To calculate $Z_{\rm eff}^{\rm (res)}$ for a molecule one must first determine the binding energy $|\varepsilon_0|$ and annihilation density ρ_{ep}. After that one should identify the vibrational excitations which can contribute to the resonant annihilation, and find D^{-1}, taking into account the symmetry of the molecule. It is also necessary to make sure that these vibrational excitations have enough coupling with the positron motion ($\Gamma_e^\nu > 1$ μeV); otherwise they will not contribute much to $Z_{\rm eff}$.

Intuition tells us that the positron motion can be coupled stronger to some simple vibrations which we shall call *doorways*. Excitation of more complicated modes or combination vibrations could then proceed through the doorways by means of anharmonic terms. As a result, the coupling strength of the doorway will be re-distributed between many complicated vibrations. In the spirit of sum rules, this means that the original emission width Γ_e^d of the doorway resonance will be shared by many narrow resonances with much smaller Γ_e^ν. On the other hand, their level density D^{-1} is much greater than that of the doorway resonances d^{-1}, so that $\Gamma_e^\nu \sim \Gamma_e^d(D/d)$. Therefore, the ratio Γ_e^ν/D in molecules with complex spectra remains approximately the same as that in simple molecules. However, as long as $\Gamma_e^\nu > \Gamma_a^\nu$, the smallness of Γ_e^ν is not limiting the $Z_{\rm eff} \propto D^{-1}$ growth, Eq. (26). Eventually, for even more complicated molecules the regime $\Gamma_e^\nu \lesssim \Gamma_a^\nu$ takes over and the rapid increase of $Z_{\rm eff}$ saturates. Experimentally, saturation of $Z_{\rm eff}$ has been observed in alkanes with $n \geq 8$.

Obviously, *ab initio* calculation of $Z_{\rm eff}$ for a large molecule is an extremely difficult problem. However, it is easy to estimate $Z_{\rm eff}^{\rm (res)}$ for simple molecules with one dominant vibrational mode. Here we can approximate the positions of the vibrational resonances by $\varepsilon_\nu = \nu\omega - \varepsilon_0$ ($\nu = 1, 2, \ldots$), where ω is the vibrational frequency of the symmetric mode of the positron-molecule compound. To find the thermally averaged $Z_{\rm eff}$ we calculate

$$\overline{Z}_{\rm eff}^{\rm (res)}(T) = \int_0^\infty \frac{e^{-k^2/2k_BT}}{(2\pi k_BT)^{3/2}} Z_{\rm eff}^{\rm (res)} 4\pi k^2 dk, \qquad (28)$$

where $Z_{\rm eff}^{\rm (res)}$ is given by Eq. (23). Assuming that the resonances are narrow, yet $\Gamma_e^\nu \gg \Gamma_a^\nu$, we obtain[14]

$$\overline{Z}_{\rm eff}^{\rm (res)}(T) = \sum_{\varepsilon_\nu > 0} \frac{8\pi^3 \rho_{ep} e^{-\varepsilon_\nu/k_BT}}{(2\pi k_BT)^{3/2}} = \frac{8\pi^3 \rho_{ep}}{(2\pi k_BT)^{3/2}} \frac{e^{-\varepsilon_0'/k_BT}}{e^{\omega/k_BT} - 1}, \qquad (29)$$

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[14] The contribution of the νth resonance is equivalent to $(2\pi^2/k)\rho_{ep}(\Gamma_e^\nu/\Gamma_\nu)\delta(\varepsilon - \varepsilon_\nu)$.

where $\varepsilon_0' < 0$ is the energy of the highest vibrationally-excited state lying *below* threshold (for $\omega > |\varepsilon_0|$, $\varepsilon_0' = \varepsilon_0$). Note that in the high-temperature limit $k_BT \gg \omega$, this formula turns into

$$\overline{Z}_{\rm eff}^{(\rm res)}(T) = \frac{2\pi^2\rho_{ep}}{\omega}\left(\frac{2}{\pi k_BT}\right)^{1/2}, \qquad (30)$$

which could also be obtained from Eq. (26) by Maxwellian averaging of $1/k$ and putting $D = \omega$.

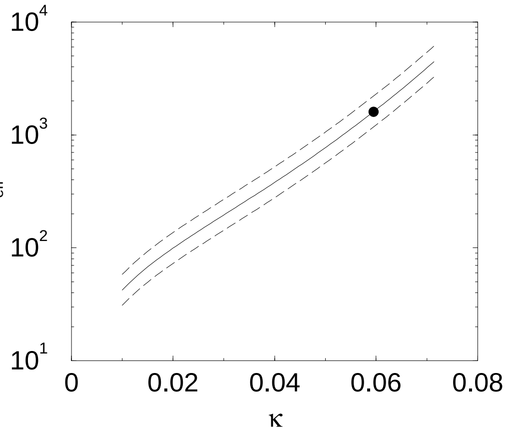

Figure 3. Dependence of $\overline{Z}_{\rm eff}^{(\rm res)}(T)$, Eq. (29), for Cl_2 at $T = 293$ K on the bound-state parameter κ. Solid line corresponds to $\omega = 560$ cm^{-1}, whereas dashed lines are for $\omega = 500$ cm^{-1} (upper) and $\omega = 620$ cm^{-1} (lower). The solid circle marks the experimental value $Z_{\rm eff} = 1600$ [52] and implies $\kappa = 0.0595$.

In Figure 3 we have applied Eq. (29) to investigate the dependence of resonant $Z_{\rm eff}$ for Cl_2 on the energy of the hypothetical e^+Cl_2 bound state. The bound-state parameter affects $\overline{Z}_{\rm eff}^{(\rm res)}(T)$ through the exponent $e^{\kappa^2/2k_BT}$, and through ρ_{ep}, via Eq. (22) with $F = 0.66$. Three curves correspond to different vibrational frequencies of e^+Cl_2: less, equal, and greater than that of Cl_2. Comparison with experiment suggests that e^+Cl_2 is bound by $\kappa^2/2 \approx 50$ meV. For such κ the direct annihilation rate should be somewhere between those of Be and Zn (Table 5), hence $Z_{\rm eff}^{(\rm dir)}$ would not exceed 200.

Equation (29) also enables one to evaluate the dependence of the resonant annihilation rates on ω. For small positron binding energies $|\varepsilon_0| < k_BT$, and "large" $\omega > k_BT$, only one lowest resonance contributes noticeably to the sum, and $\overline{Z}_{\rm eff}^{(\rm res)}(T)$ depends on ω exponentially. To emphasize this strong dependence in Figure 4, other parameters in Eq.

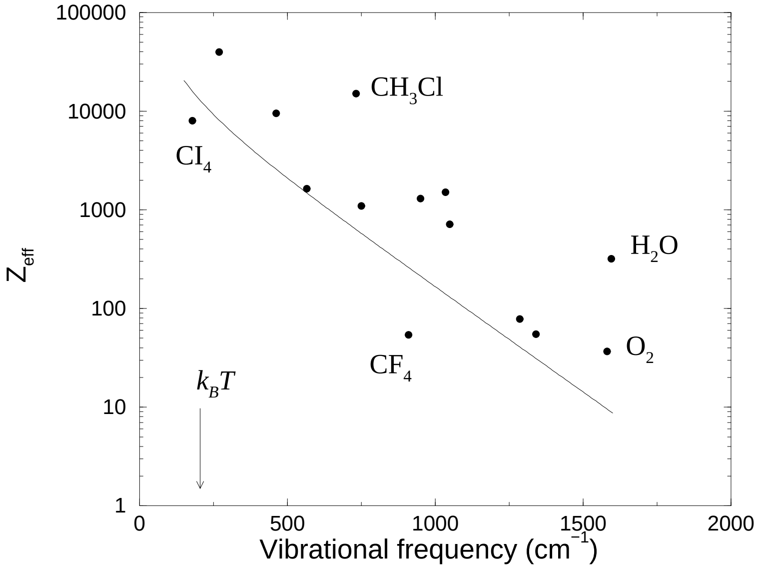

Figure 4. $Z_{\rm eff}$ of simple molecules as a function of the lowest vibrational frequency ω of the fully symmetric mode (A_1, A_g) [49, 54]. The molecules included, in the order of decreasing ω, are H_2O, O_2, CO_2, N_2O, CH_3F, CH_3OH, NH_3, CF_4, NO_2, CH_3Cl, Cl_2, CCl_4, CBr_4, and CI_4. Solid curve is $\overline{Z}_{\rm eff}^{\rm (res)}(T)$ of Eq. (29), obtained using $\rho_{ep} = \rho_{\rm Ps}$ and $|\varepsilon_0| \ll k_BT$.

(29) are kept constant: $\rho_{ep} = \rho_{\rm Ps}$ and $|\varepsilon_0| \ll k_BT$. Apart from the points for CF_4 and H_2O, the rest of the data seem to correlate well with the slope of the curve. For molecules on the high-frequency side of the graph, the contribution of resonant annihilation is small. In fact they probably do not bind positrons, and their $Z_{\rm eff}$ can be explained in terms of direct annihilation. It is conceivable that resonant annihilation contributes to $Z_{\rm eff}$ in H_2O, if a stronger positron binding lowers the resonance towards thermal positron energies. The datum for CF_4 again points out that resonant annihilation does not contribute to $Z_{\rm eff}$, for want of positron binding. For all other molecules with $\omega < 1000$ cm^{-1} the observed annihilation rates are probably sums of $Z_{\rm eff}^{\rm (dir)}$ and $Z_{\rm eff}^{\rm (res)}$, the latter becoming increasingly important as ω becomes smaller.

5. SUMMARY AND OUTLOOK

Ideas outlined in this paper provide a solid framework for the description and understanding of positron annihilation on molecules. The two basic annihilation mechanisms, direct and resonant, should be capable of describing the whole variety of phenomena associated with this process, such as large values of Z_{eff}, their rapid increase with the size of the molecule, and strong chemical sensitivity. Complete understanding of resonant annihilation will require solving several difficult problems, namely those of positron binding to molecules, energy transfer between the positron and vibrational degrees of freedom, and formation of complex molecular vibrational resonances.

Resonant annihilation has much in common with the formation of long-lived negative ions and dissociative attachment in low-energy electron collisions with molecules. These processes are believed to be mediated by vibrational Feshbach resonances, but they are also far from being completely understood. From this point of view, enhanced annihilation in positron-molecule collisions is a unique signature of the resonant nature of the process.

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[51] I believe that Cl_2 may well be the simplest *nonpolar* molecule likely to form a bound state with the positron. Its dipole polarisability $\alpha_d = 31.1$ au [48] is greater than that of Xe, and it has a rather low ionisation potential $I = 11$ eV, which promotes additional attraction due to virtual Ps formation.

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[53] It is instructive to juxtapose electron and positron interaction with SF_6. This molecule is known as "electron scavenger", as it captures electrons into extremely long-lived negative ion states [27]. The underlying mechanism must be electron binding (SF_6 has a large electron affinity), accompanied by excitation of a dense spectrum of very narrow multimode vibrational resonances.

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