

Positron Annihilation in Molecules by Capture into Vibrational Feshbach Resonances of Infrared-Active Modes

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Enhanced positron annihilation on polyatomic molecules is a long-standing and complex problem. We report the results of calculations of resonant positron annihilation on methyl halides. A free parameter of our theory is the positron binding energy. A comparison with energy-resolved annihilation rates measured for CH_3F , CH_3Cl , and CH_3Br [L. D. Barnes *et al.*, Phys. Rev. A **74**, 012706 (2006)] shows good agreement and yields estimates of the binding energies.

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In this Letter we calculate the positron-molecule annihilation rate due to resonant capture of positrons by infrared-active vibrational modes and observe good agreement with recent experimental data for methyl halides [1].

When a fast positron interacts with matter, it undergoes a quick succession of ionizing and other inelastic collisions and slows down to eV or thermal energies before annihilation. The low-energy positron annihilation rate in a gas with number density, n , is usually parametrized as

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

where σ_a is the annihilation cross section, v is the positron velocity, c is the speed of light, r_0 is the classical electron radius, and Z_{eff} is an *effective number of electrons* per gas atom or molecule, which contribute to annihilation [2,3]. Originally, Z_{eff} was introduced in expectation that the annihilation rate would be in proportion to the number of target electrons, Z . However, early experiments [4–6] and later systematic studies [7–9] found that for many polyatomic molecules Z_{eff} exceeded Z by orders of magnitude. It also showed strong chemical sensitivity and rapid growth with molecular size (for a review, see [10]).

Explanations of high molecular Z_{eff} were sought in terms of positron virtual or weakly bound states [11], resonances [12,13], long-lived vibrationally excited positron-molecule complexes [8], and virtual Ps formation [14]. At the same time, annihilation calculations which neglected molecular vibrations failed to reproduce “anomalous” Z_{eff} for polyatomics [15,16], but gave evidence that Z_{eff} depend on the molecular geometry [17].

These efforts highlight the fact that positron-molecule annihilation is a complex problem. Nevertheless, a theory developed in Refs. [18–20] provides a framework for analyzing this phenomenon. There are two basic mechanisms of positron annihilation, direct and resonant. The direct mechanism applies to both atoms and molecules and involves annihilation of an incident positron “in flight.” Its contribution is enhanced when a low-lying virtual or weakly bound positron state is present, leading to Z_{eff} up to 10^3 for room-temperature positrons [18,19].

Resonant annihilation occurs for molecules capable of binding the positron. To be captured into a bound state, the positron energy must be absorbed by a vibrational excitation of the positron-molecule complex. This gives rise to a vibrational Feshbach resonance (VFR) at the incident positron energy $\varepsilon = E_\nu + \varepsilon_0$, where E_ν is the vibrational excitation energy, and $\varepsilon_0 < 0$ is the positron bound state energy. The positron bound in the VFR can annihilate (or undergo detachment). The probability of annihilation is proportional to the resonance lifetime.

For nonmonoenergetic positrons and closely spaced resonances, their contribution to Z_{eff} is proportional to the vibrational level density at $E \approx \varepsilon - \varepsilon_0$ [18,19]. If the positron VFR were due to excitation of fundamentals alone, this density would be proportional to the number of modes. Experimental Z_{eff} show much faster increase (e.g., $Z_{\text{eff}} = 3500$, 11 300, and 37 800 for C_3H_8 , C_4H_{10} , and C_5H_{12} , respectively). This means that positron attachment involves excitation of overtones and combination vibrations. Large Z_{eff} are then related to high total vibrational spectrum densities in the polyatomics.

The important role of vibrations was recently verified by measuring the energy dependence of Z_{eff} at sub-eV energies with a high-resolution positron beam [21,22]. These experiments uncovered peaks in Z_{eff} , whose energies corresponded to those of molecular vibrational modes. In particular, for all alkanes larger than methane, Z_{eff} displayed a prominent C-H maximum. Its downshift from the C-H mode energy (0.37 eV) provided a measure of the positron binding energy [23]. Observation of such peaks means that excited fundamentals act as vibrational doorway states [20], leading to multimode vibrations through intramolecular vibrational relaxation (IVR).

Therefore, to compute Z_{eff} for polyatomics, one must account for strong electron-positron correlations and positron binding, the interaction between positronic and vibrational degrees of freedom and intramolecular vibrational mixing. This makes *ab initio* calculations of high molecular Z_{eff} very difficult. However, as we show below, for

small polyatomics some basic features of resonant annihilation can be tested by relatively simple calculations.

The resonant part of the annihilation cross section can be written using the Breit-Wigner formalism [19,20,24],

$$\sigma_a = \frac{\pi}{k^2} \sum_{\nu} \frac{g_{\nu} \Gamma_{\nu}^a \Gamma_{\nu}^e}{(\varepsilon - E_{\nu} - \varepsilon_0)^2 + \Gamma_{\nu}^2/4}, \quad (2)$$

where Γ_{ν}^a , Γ_{ν}^e , and Γ_{ν} are the annihilation, elastic, and total widths of ν th resonance, g_{ν} is its degeneracy, and k is the positron momentum (atomic units are used). The annihilation width of the positron bound state is proportional to the average electron density at the positron, ρ_{ep} [3,18,19],

$$\Gamma_{\nu}^e = \pi r_0^2 c \rho_{\text{ep}}. \quad (3)$$

From Eqs. (1) and (2), the resonant Z_{eff} is given by

$$Z_{\text{eff}}^{(\text{res})} = \frac{\pi}{k} \rho_{\text{ep}} \sum_{\nu} \frac{g_{\nu} \Gamma_{\nu}^e}{(\varepsilon - E_{\nu} - \varepsilon_0)^2 + \Gamma_{\nu}^2/4}. \quad (4)$$

We will now use this equation to calculate the contribution of infrared-active modes to $Z_{\text{eff}}^{(\text{res})}$.

Consider a compact polyatomic molecule that can bind the positron with a small binding energy $|\varepsilon_0| \equiv \kappa^2/2 \ll 1$ eV. The wave function of the bound positron is very diffuse and behaves as $\varphi_0 = A r^{-1} e^{-\kappa r}$ outside the molecule. Since large distances dominate, the normalization constant is given by $A \simeq (\kappa/2\pi)^{1/2}$ [25].

Suppose that the vibrational modes in this small-sized polyatomic are not mixed with overtones or combination vibrations. Given the smallness of the binding energy, the vibrational excitation energies of the positron-molecule complex should be close to the fundamental frequencies ω_{ν} of the neutral molecule. In this case the sum in Eq. (4) is over the modes ν , and $E_{\nu} \approx \omega_{\nu}$. Some (or even all) of these modes can be infrared active. The positron capture into such excited states is mediated by the long-range dipole coupling. This allows one to calculate their contribution to $Z_{\text{eff}}^{(\text{res})}$.

Consider a positron with momentum \mathbf{k} incident on the molecule in the vibrational ground state $\Phi_0(\mathbf{R})$, where \mathbf{R} represents all the molecular coordinates. If $k^2/2 \approx \omega_{\nu} + \varepsilon_0$, the positron can be captured in the VFR, where it is bound to the molecule in a vibrationally excited state $\Phi_{\nu}(\mathbf{R})$. The corresponding width Γ_{ν}^e can be found from

$$\Gamma_{\nu}^e = 2\pi \int |A_{\nu\mathbf{k}}|^2 \delta(k^2/2 - \omega_{\nu} - \varepsilon_0) \frac{d^3k}{(2\pi)^3}, \quad (5)$$

where $A_{\nu\mathbf{k}}$ is the capture amplitude. We calculate it by using a method similar to the Born-dipole approximation [26,27], as

$$\begin{aligned} A_{\nu\mathbf{k}} &= \int \varphi_0(\mathbf{r}) \Phi_{\nu}^*(\mathbf{R}) \frac{\hat{\mathbf{d}} \cdot \mathbf{r}}{r^3} e^{i\mathbf{k} \cdot \mathbf{r}} \Phi_0(\mathbf{R}) d\mathbf{r} d\mathbf{R} \\ &= \frac{4\pi i}{3} \frac{\mathbf{d}_{\nu} \cdot \mathbf{k}}{\sqrt{2\pi\kappa}} {}_2F_1\left(\frac{1}{2}, 1; \frac{5}{2}; -\frac{k^2}{\kappa^2}\right), \end{aligned} \quad (6)$$

where $\hat{\mathbf{d}}$ is the dipole moment operator for the molecule, $\mathbf{d}_{\nu} = \langle \Phi_{\nu} | \hat{\mathbf{d}} | \Phi_0 \rangle$, and ${}_2F_1$ is the hypergeometric function [28]. Substitution of Eq. (6) into Eq. (5) gives

$$\Gamma_{\nu}^e = \frac{16\omega_{\nu} d_{\nu}^2}{27} h(\xi), \quad (7)$$

where $h(\xi) = \xi^{3/2} (1 - \xi)^{-1/2} [{}_2F_1(\frac{1}{2}, 1; \frac{5}{2}; -\xi/(1 - \xi))]^2$ is a dimensionless function of $\xi = 1 + \varepsilon_0/\omega_{\nu}$, such that $\xi(0) = \xi(1) = 0$, and $h_{\text{max}} \approx 0.75$ at $\xi \approx 0.89$.

Equation (7) shows that the elastic width of a positron VFR for an infrared active mode is basically determined by its frequency ω_{ν} and transition dipole amplitude d_{ν} , known from infrared absorption measurements [29].

For weakly bound positron states the density ρ_{ep} is a linear function of κ [19]. It can be estimated as

$$\rho_{\text{ep}} = (F/2\pi)\kappa, \quad (8)$$

with $F \approx 0.66$ [19]. The same constant characterizes the contribution of direct annihilation, $Z_{\text{eff}}^{(\text{dir})} \simeq F/(\kappa^2 + k^2)$ [19]. It is enhanced at small positron momenta by the presence of a weakly bound (or virtual) state [11,30].

In a recent paper [1], measurements of Z_{eff} for CH_3Cl and CH_3Br using a cold trap-based positron beam have been reported. The energy dependence of Z_{eff} for these molecules (and CH_3F measured earlier [22]) shows peaks close to the vibrational mode energies. This points to an important contribution of resonant annihilation in all three molecules, although the maximum Z_{eff} value for CH_3F (250) is much lower than those for CH_3Cl and CH_3Br (1600 and 2000, respectively).

These molecules have C_{3v} symmetry, and all six of their vibrational modes are infrared active (see Table I for CH_3Cl). Methyl halides are also relatively small, which means that IVR may not take place [31]. This makes them ideal for application of our theory. Equations (4), (7), and (8) allow one to calculate the contribution of *all* VFR to $Z_{\text{eff}}^{(\text{res})}$, and the only free parameter of the theory, i.e., the positron binding energy, can be chosen by comparison with experimental Z_{eff} .

In order to do this, $Z_{\text{eff}}^{(\text{res})}$ from Eq. (4) must be averaged over the energy distribution of the positron beam [22]. The latter can be modeled by a combination of the Gaussian distribution in the longitudinal direction (z) and Maxwellian distribution in the transversal direction (\perp).

TABLE I. Characteristics of the vibrational modes of CH_3Cl .

Mode	Symmetry	g_{ν}	ω_{ν}^a (meV)	d_{ν} (a.u.)	$\omega_{\nu} d_{\nu}^2$ (a.u.)
ν_1	a_1	1	363	0.0191	4.87×10^{-6}
ν_2	a_1	1	168	0.0176	1.91×10^{-6}
ν_3	a_1	1	91	0.0442	6.52×10^{-6}
ν_4	e	2	373	0.0099	1.34×10^{-6}
ν_5	e	2	180	0.0162	1.74×10^{-6}
ν_6	e	2	126	0.0111	5.66×10^{-7}

^aMode energies ω_{ν} and dipole amplitudes d_{ν} from Ref. [29].

The corresponding probability density of the total positron energy, $\varepsilon_{\perp} + \varepsilon_z$, is

$$f_{\varepsilon}(\varepsilon_{\perp}, \varepsilon_z) = \frac{1}{k_B T_{\perp} \sqrt{2\pi\sigma^2}} \exp\left[-\frac{\varepsilon_{\perp}}{k_B T_{\perp}} - \frac{(\varepsilon_z - \epsilon)^2}{2\sigma^2}\right],$$

where k_B is the Boltzmann constant, T_{\perp} is an effective transversal temperature of the beam, ϵ is the mean longitudinal energy of the positrons, as measured by the retarding potential analyzer, and $\sigma = \delta_z/\sqrt{8\ln 2}$, δ_z being the full width at half maximum. The values of $k_B T_{\perp}$ and δ_z are taken from experiment to be 25 meV.

The averaging, $\bar{Z}_{\text{eff}}^{(\text{res})}(\epsilon) = \int Z_{\text{eff}}^{(\text{res})} f_{\varepsilon}(\varepsilon_{\perp}, \varepsilon_z) d\varepsilon_{\perp} d\varepsilon_z$, can be done analytically, since the widths of the resonances, $\Gamma_{\nu} = \Gamma_{\nu}^e + \Gamma_{\nu}^a$, are small compared to the energy spread of the positron beam. Indeed, values from the last column of Table 1 show that the elastic widths of the VFR are less than 0.1 meV. Typical annihilation widths are even smaller. For example, for a binding energy of 10 meV ($\kappa = 0.027$ a.u.), Eqs. (3) and (8) yield $\Gamma_{\nu}^a = 3 \times 10^{-9}$ a.u. = 0.1 μeV . These estimates also show that $\Gamma_{\nu} \approx \Gamma_{\nu}^e$, i.e., that the total width of the resonance is dominated by its elastic width.

Hence, to integrate over ε_{\perp} and ε_z we replace the Breit-Wigner profiles in Eq. (4) by δ functions and obtain

$$\bar{Z}_{\text{eff}}^{(\text{res})}(\epsilon) = 2\pi^2 \rho_{\text{ep}} \sum_{\nu} \frac{g_{\nu} \Gamma_{\nu}^e}{k_{\nu} \Gamma_{\nu}} \Delta(\epsilon - \varepsilon_{\nu}), \quad (9)$$

where $\varepsilon_{\nu} = k_{\nu}^2/2 = \omega_{\nu} + \varepsilon_0$ is the resonance energy, and

$$\Delta(E) = \frac{1}{k_B T_{\perp}} \exp\left[\frac{\sigma^2}{2(k_B T_{\perp})^2}\right] \exp\left(\frac{E}{k_B T_{\perp}}\right) \times \left\{1 + \Phi\left[-\frac{1}{\sqrt{2}}\left(\frac{E}{\sigma} + \frac{\sigma}{k_B T_{\perp}}\right)\right]\right\}, \quad (10)$$

with $\Phi(x)$ being the standard error function.

The function $\Delta(E)$ is a convolution of the δ function with the positron energy distribution. It describes the appearance of a narrow resonance when measured with the trap-based positron beam and is shown in Fig. 1. Because of the transversal energy component, its maximum is downshifted by 12 meV from the true resonance position. The shape of $\Delta(E)$ is also markedly asymmetric, with an extended low-energy tail. It agrees well with those of the observed C-H peaks [21,22]. Note that the positron energy distribution was taken into account in experiment by assuming a 16 meV difference between the positron total and longitudinal energies [22].

In Fig. 2 we compare the theoretical Z_{eff} obtained as a sum of the beam-energy-averaged $Z_{\text{eff}}^{(\text{dir})}$ and $\bar{Z}_{\text{eff}}^{(\text{res})}$ from Eq. (9), with measured Z_{eff} for methyl halides [1,22]. Theoretical curves have been obtained using the binding energy of $|\varepsilon_0| = 0.3, 25,$ and 40 meV, for CH_3F , CH_3Cl , and CH_3Br , respectively.

Given the complexity of the problem and the fact that ε_0 is the only free parameter in the calculation, the agreement between theory and experiment in Fig. 2 is remarkable. In

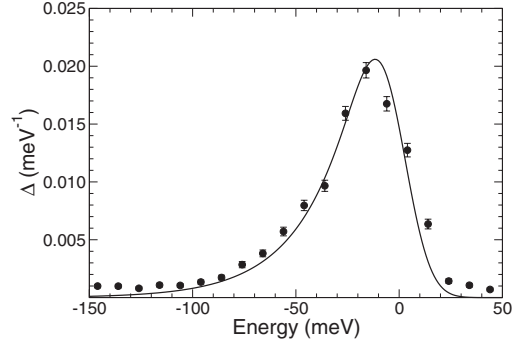


FIG. 1. Comparison of the resonance shape function $\Delta(E)$, for $k_B T_{\perp} = \delta_z = 25$ meV (curve) with the measured C-H peak in propane (circles) [21,22]. For comparison, experimental Z_{eff} has been scaled vertically and shifted horizontally.

accord with Eq. (9), every vibrational mode gives rise to a VFR, whose relative magnitude is determined by the factor g_{ν}/k_{ν} (since $\Gamma_{\nu}^e/\Gamma_{\nu} \approx 1$). On the positron longitudinal energy scale, the resonances are downshifted from the mode energies by the positron binding energy and a further 12 meV due to the positron energy distribution.

Besides determining the resonance positions, the binding energy also affects the overall magnitude of $Z_{\text{eff}}^{(\text{res})}$ via $\rho_{\text{ep}} \propto |\varepsilon_0|^{1/2}$ [Eq. (8)]. Hence, the smallness of Z_{eff} in

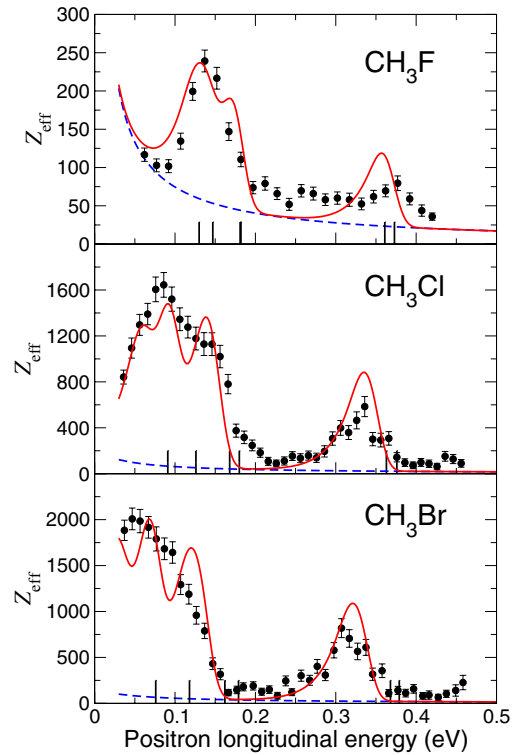


FIG. 2 (color online). Comparison between experimental Z_{eff} (●, Ref. [1]) and theoretical Z_{eff} (solid curves) for the positron binding energies of $|\varepsilon_0| = 0.3$ meV (CH_3F), 25 meV (CH_3Cl), and 40 meV (CH_3Br). Dashed curves show $Z_{\text{eff}}^{(\text{dir})}$. Vertical bars show the energies of molecular fundamentals.

CH₃F in comparison with those of CH₃Cl and CH₃Br is related to the weakness of its binding. This is in turn related to the smaller dipole polarizability and higher ionization potential of fluoromethane, which make it less attractive for the positron.

Note that the infrared absorption strengths of the modes and the corresponding elastic widths, $\Gamma_\nu^e \sim \omega_\nu d_\nu^2$, may vary considerably from mode to mode. On the other hand, the contribution of different modes to Z_{eff} are similar, apart from energy shift and g_ν/k_ν factor. As a result, the energy dependence of Z_{eff} has little resemblance to the molecular infrared absorption spectra [1]. The relation $\Gamma_\nu \approx \Gamma_\nu^e$ also means that the contributions of the VFR are not sensitive to the exact values of the elastic widths. Therefore, our use of the ‘‘Born-dipole’’ approximation in the derivation of Eq. (7) is not expected to lead to sizeable errors in $Z_{\text{eff}}^{(\text{res})}$.

In conclusion, we have presented a theory of positron annihilation by capture into vibrational resonances of infrared-active modes. It agrees well with measured Z_{eff} for methyl halides and yields estimates of the positron binding energies for these molecules.

This theory can also be used to investigate the contribution of infrared-active-mode VFRs to Z_{eff} in other small polyatomics that can bind positrons. Such calculations will likely underestimate the Z_{eff} because the resonances associated with other (nondipole) modes may contribute just as much, as long as their elastic widths are greater than the annihilation width.

In molecules where multiquantum vibrations are coupled by anharmonicity, the number of VFRs populated by positron capture will be greatly increased, leading to much higher Z_{eff} . However, the same coupling will also allow the VFR to decay by positron emission to vibrationally excited states of the molecule. This will increase the total resonance widths, thereby reducing their individual contributions. Calculation of Z_{eff} for molecules with IVR is the next big challenge for the theory.

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