Feshbach projection operator approach to positron annihilation

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We present a theory of vibrationally enhanced positron annihilation on molecules based on the Feshbach projection operator formalism. A key aspect of the present approach is the fact that no direct vibrational excitation is assumed, i.e., the attachment mechanism is electronic in nature, arising from positron-electron correlation-polarization forces, and energy transfer to the nuclei essentially follows from the difference between the potential-energy surfaces of the isolated target and the positron-molecule compound; moreover, no *a priori* assumption is made on the character of the transient (bound or virtual state). An approximate relation between the annihilation parameter Z_{eff} and the vibrationally summed cross section is presented, as well as a hierarchy of approximations that may allow for elaborate model calculations. We also discuss how important aspects of the annihilation process are taken into account in the present theory, such as isotope effects, vibrational energy redistribution and relative strengths among vibrational resonances. For completeness, semiempirical model calculations for acetylene and ethylene are presented. Despite the stringent approximations employed in this simplest version of the theory, fair agreement with experimental data was obtained in the vicinity of $0 \rightarrow 1$ thresholds.

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I. INTRODUCTION

The annihilation of slow positrons on molecules has attracted considerable interest for decades. Early measurements at room temperature [1,2] already pointed out that annihilation rates (λ) in molecular gases [3],

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

could be very high. In the expression above, r_0 is the classical electron radius, c is the velocity of light, n is the gas density, and

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i} \langle \Psi_{k_i}^{(+)} | \sum_{j=1}^{Z} \delta(\mathbf{r}_j - \mathbf{r}_p) | \Psi_{k_i}^{(+)} \rangle \tag{2}$$

is the (angle-averaged) annihilation parameter [4], where $|\Psi_{k_i}^{(+)}\rangle$ is the outgoing scattering wave function, Z is the number of electrons in the molecule, and k_i is the magnitude of the incident positron wave vector, $E = k_i^2/2$. If positron-electron correlation-polarization forces are small, Z_{eff} should be of the order of Z. The large Z_{eff} values were thus interpreted as the effective number of electrons taking part in annihilation (i.e., a measure of correlation effects). This picture does not provide a sound interpretation of more recent experiments with thermalized positrons, since Z_{eff} may exceed the number of electrons by orders of magnitude (see Surko *et al.* [5] and references therein).

Early attempts to explain the high annihilation rates relied on weakly bound [6] and virtual states [7] and recent scattering calculations indeed support the existence of low-lying virtual states for small hydrocarbons [8,9] that become bound states upon stretching of molecular bonds [9,10]. Though Z_{eff} values are enhanced by electron-positron correlation effects, energy-resolved experiments undoubtedly pointed out that very high annihilation rates arise from vibrational resonances [11], as proposed by Gribakin [12]. Several phenomenological models of vibrationally enhanced annihilation have been proposed to explain the rich experimental data (see [13] and references therein) and the recent one by Gribakin and Lee [14] could successfully describe energy-resolved Z_{eff} for polar targets, having only infrared-active vibrational modes.

In this work, we propose a Feshbach projection operator (FPO) approach to positron annihilation on molecules. The FPO formalism has long been applied to resonant electron-molecule collisions [15] and was recently employed in studies of vibrationally inelastic positron scattering [10,16]. Since this approach is based on a formal theory, it provides a consistent hierarchy of approximations and innately incorporates several important aspects of vibrational couplings, such as isotope effects, overtones, combination vibrations, vibrational energy redistribution, and relative coupling strengths among different vibrational modes. The formalism describes the scattering process as a discrete state (trapped positron) coupled to a continuum (free positron). The positron, initially in the continuum, has a finite probability of being captured in the discrete state, which subsequently decays into a scattering state. If the capture (decay) probability is small, the temporary positron-molecule compound will be long lived, allowing for significant nuclear motion during the collision. These molecular vibrations will take place on a potential-energy surface (PES) modified by the trapped positron, as illustrated in Fig. 1. Any stationary vibrational eigenstate of the isolated target (vibrational entrance channel) will give rise to a traveling-wave packet on the positron-molecule PES and hence to constructive interference at the stationary energies (vibrational eigenvalues) of the positron-molecule compound. Long-lived temporary ions favor constructive interference and give rise to narrow vibrational resonances, in much the same way as long-lived states give rise to sharp spectral lines. These narrow vibrational resonances, arising from the electronic capture of the positron, significantly enhance the energy-resolved annihilation rates (see below). A

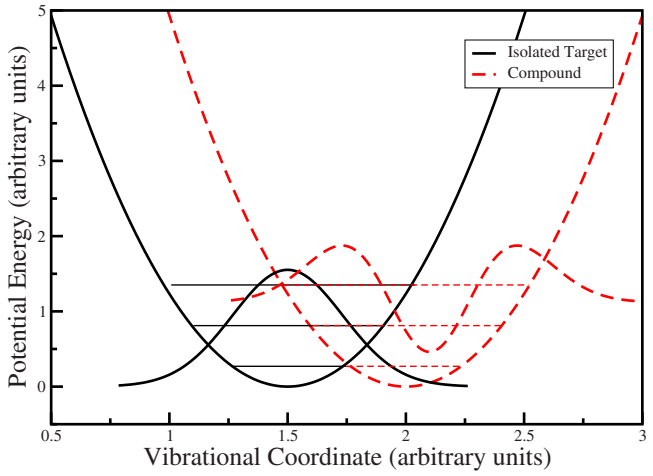

FIG. 1. (Color online) Schematic representation of the vibrationally enhanced annihilation mechanism. The target is initially in the vibrational ground state (solid black line) and positron attachment instantaneously launches the nuclei onto the potential surface of the positron-molecule compound (red dashed line). Due to the differences between these potentials, the vibrational eigenstate of the target gives rise to a nonstationary wave packet on the transient surface whose imaginary part is not shown.

key aspect of the present approach is the fact that no direct vibrational excitation is assumed, i.e., the process is not understood on the basis of a positron-nucleus interaction. The attachment mechanism is electronic in nature, arising from positron-electron correlation-polarization forces, and energy transfer to the nuclei essentially follows from the difference between the potentials of the isolated target and the compound system. This is consistent with the fact that target electrons are expected to respond faster to the positron field (due to the larger energy spacings) than nuclear degrees of freedom. Finally, we make no *a priori* assumption on the character of the positron-molecule compound; bound or virtual states, as well as electronic resonances, if these exist at all, could trigger the nonstationary nuclear wave packet, thus enhancing the annihilation rate on the molecular gas of interest.

This paper is outlined as follows. In Sec. II, we present a heuristic view of the annihilation process, providing an intuitive picture of the mechanism. Section III focuses on the formal aspects, addressing both the general theory and a few working approximations. A model calculation for small hydrocarbons is discussed in Sec. V and our conclusions are given in Sec. VI.

II. MECHANISM: A HEURISTIC VIEW

In this section, we outline the physical picture underlying the formalism presented in the next section. The nuclear motion on the complex PES of the positron-molecule temporary state is addressed from a heuristic standpoint as follows. Positron capture launches the nuclei onto a modified potential surface, $V_0 \xrightarrow{e^+} V_{\text{cap}}$, where V_0 is the PES of the target ground state (Z electrons) and V_{cap} is the potential surface of the $(Z+1)$-particle state comprising the target electrons and the positron (see Fig. 1). Since this electron-positron state ($|\phi_{\text{cap}}\rangle$) is unstable against positron detachment, its PES should be modified accordingly. The motion of the nuclei on the potential surface of this metastable state may be obtained, to a first approximation, from the time-dependent Schrödinger equation [17]

$$i\frac{\partial}{\partial t}|\xi(t)\rangle = \left[T_N + V_{\text{cap}} - \frac{i}{2}\Gamma_{\text{cap}}\right]|\xi(t)\rangle, \tag{3}$$

where T_N is the kinetic energy of the nuclei and the width Γ_{cap} accounts for the finite lifetime of the compound state. Positron attachment gives rise to a nonstationary wave packet $|\xi(t)\rangle$ on the potential surface of the compound state subjected to the initial condition [18]

$$|\xi(t \to 0^+)\rangle = \sqrt{\frac{\Gamma_{\text{cap}}}{2\pi}}|\eta_0\rangle, \tag{4}$$

where $\sqrt{\Gamma_{\text{cap}}/2\pi}$ is the capture amplitude and $|\eta_0\rangle$ is the vibrational ground state of the isolated target (more generally, the vibrational entrance channel). Assuming, for simplicity, constant Γ_{cap} and a single vibrational mode, the solution of Eq. (3) may be easily obtained from the vibrational spectrum of the compound Hamiltonian, $(T_N+V_{\text{cap}})|\chi_\nu\rangle=\varepsilon_\nu|\chi_\nu\rangle$, such that

$$|\xi(t)\rangle = \sqrt{\frac{\Gamma_{\text{cap}}}{2\pi}}\sum_\nu |\chi_\nu\rangle\exp\left[-i\varepsilon_\nu t - \frac{\Gamma_{\text{cap}}t}{2}\right]\langle\chi_\nu|\eta_0\rangle. \tag{5}$$

Equation (5) can be transformed to the energy domain

$$|\xi(E)\rangle = \sqrt{\frac{\Gamma_{\text{cap}}}{2\pi}}\sum_\nu \frac{c_{\nu 0}}{(E-\varepsilon_\nu)+i\Gamma_{\text{cap}}/2}|\chi_\nu\rangle, \tag{6}$$

where E is the incident positron energy and $c_{\nu 0}=\langle\chi_\nu|\eta_0\rangle$ is the Franck-Condon (FC) overlap between the target vibrational ground state and the νth eigenstate of the compound. The annihilation parameter may be readily obtained by substituting the total wave function $|\Psi\rangle=|\phi_{\text{cap}}\rangle|\xi(E)\rangle$ in Eq. (2),

$$Z_{\text{eff}} = \frac{\pi}{k_i}\rho_{\text{cap}}\sum_\nu |c_{\nu 0}|^2\frac{\Gamma_{\text{cap}}}{(E-\varepsilon_\nu)^2+\Gamma_{\text{cap}}^2/4}, \tag{7}$$

where

$$\rho_{\text{cap}} = \langle\phi_{\text{cap}}|\sum_{j=1}^{Z}\delta(\mathbf{r}_j-\mathbf{r}_p)|\phi_{\text{cap}}\rangle \tag{8}$$

is the electron density at the positron. In deriving Eq. (7), we have implicitly dropped all angular dependences and assumed that the scattering wave function at large positron-molecule separations does not contribute to annihilation.

At this point, two aspects should be emphasized. First, the key assumption underlying Eq. (7) was the existence of a Born-Oppenheimer (BO) electron-positron state, $|\phi_{\text{cap}}\rangle$, and the vibrational resonances therein arise from nuclear motion on the potential surface of this metastable state. This picture of electronic attachment followed by energy transfer to vibrational degrees of freedom is widely employed in resonant electron scattering [15] and is consistent with a faster re-

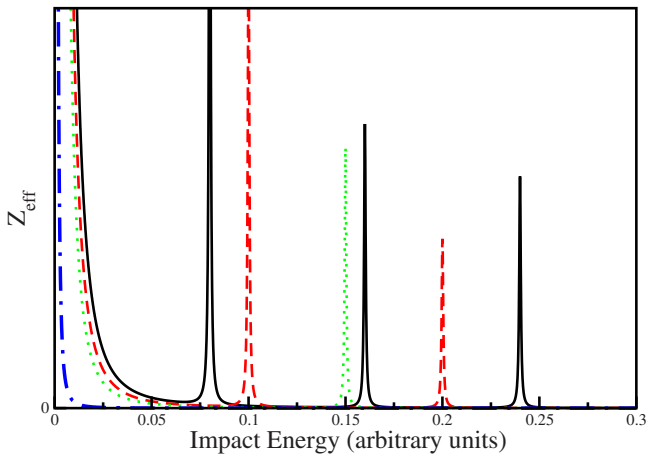

FIG. 2. (Color online) Schematic representation of the contribution of vibrational coupling strengths to the annihilation parameter Z_{eff}. In the limit of vanishing couplings, the potential-energy surfaces of the isolated target and positron-molecule compound can only differ by a constant, giving rise to a single resonance at $\nu=0$, corresponding to $c_{\nu 0}=\delta_{\nu 0}$ in Eq. (7) (blue dot-dashed line). Larger coupling strengths arise from significant differences between the compound and target potentials, giving rise to higher-lying resonances: $\nu=0,1$ (green dotted line), $\nu=0,1,2$ (red dashed line), and $\nu=0,1,2,3$ (solid black line).

sponse of the light electrons. In addition, the analogy with absorption spectroscopy should be pointed out. Electronic radiative transitions instantaneously launch the nuclei onto an excited-state potential, $V_0 \overset{h\nu}{\longrightarrow} V_{\mathrm{exc}}$, whose vibrational levels give rise to vibronic bands. To a first approximation, the intensity of these bands arises from the FC factors between the vibrational eigenstates of V_0 and V_{exc} and the widths are related to the lifetimes of the excited states $(1/\Gamma_{\mathrm{exc}})$. In much the same way, positron capture gives rise to resonances on all vibrational eigenstates of the positron-molecule compound, though with relative strengths tuned by the FC factors $|c_{\nu 0}|^2$. If positron attachment barely affects the potential surface, $V_{\mathrm{cap}} \simeq V_0$, a single resonance for $\nu=0$ will be coupled since $c_{\nu 0} \simeq \delta_{\nu 0}$. If the potentials significantly differ, several resonances will be coupled since $|\eta_0\rangle = \Sigma_\nu c_{\nu 0} |\chi_\nu\rangle$. This behavior is illustrated in Fig. 2.

III. THEORY

A. Feshbach projection operator formalism

The annihilation mechanism outlined in the previous section can be stated on formal grounds with the help of the projection operator approach of Feshbach. The application of the FPO formalism [19] to vibrational excitation and dissociative attachment is described in details elsewhere [15,18,20–22], so only the main features will be given here. The Hamiltonian of the positron-molecule system can be written as

$$H = T_N + T_p + H_0 + V \equiv T_N + H_{\mathrm{ele}}, \tag{9}$$

where T_N and T_p are the kinetic energies of the nuclei and the positron, respectively, V is the positron-molecule interaction potential, and H_0 is the electronic Hamiltonian of the isolated target (including nuclear repulsion). The formalism relies on a discrete positron-electron state $|\phi_d\rangle$ parametrically dependent on the nuclear coordinates in the BO sense and orthogonal to a set of continuum states $\{|\phi_{\mathbf{k}}\rangle\}$. This uniquely defines the projection operators $Q=|\phi_d\rangle\langle\phi_d|$ and $P=(1-Q)$, thus allowing for a decomposition of the total scattering wave function according to $|\Psi^{(+)}_{\mathbf{k}_i}\rangle = |\Psi_P\rangle + |\Psi_Q\rangle$, with $|\Psi_P\rangle = P|\Psi^{(+)}_{\mathbf{k}_i}\rangle$, and

$$|\Psi_Q\rangle = Q|\Psi^{(+)}_{\mathbf{k}_i}\rangle = |\xi_d\rangle|\phi_d\rangle, \tag{10}$$

where $|\xi_d\rangle$ is the nuclear wave function on the discrete state potential. The $(Z+1)$-particle state $|\phi_d\rangle$ can be identified with $|\phi_{\mathrm{cap}}\rangle$, as $|\xi_d(t)\rangle$ with $|\xi(t)\rangle$ in the phenomenological model. The width Γ_{cap} can also be stated in terms of the coupling between the discrete and continuum states (see below) and the real-potential surface V_{cap} can be related, to a first approximation [23], with the energy expectation value $\langle\phi_d|H_{\mathrm{ele}}|\phi_d\rangle$.

The discrete-continuum coupling is strictly electronic, $QHP=QH_{\mathrm{ele}}P$, since $[T_N,Q]=[T_N,P]=0$, and the formal solutions for the projected wave functions are well known [18–20],

$$|\Psi_Q\rangle = \frac{1}{Q(E-H)Q} QH_{\mathrm{ele}}P|\Psi_P\rangle, \tag{11}$$

and

$$|\Psi_P\rangle = |\eta_{\nu_i}\rangle|\phi_{\mathbf{k}_i}\rangle + \frac{1}{P(E-H)P} PH_{\mathrm{ele}}Q|\Psi_Q\rangle, \tag{12}$$

where η_{ν_i} denotes the target's vibrational entrance channel and $|\phi_{\mathbf{k}_i}\rangle$ is a scattering eigenstate of $PH_{\mathrm{ele}}P$.

The projection of the wave function onto P and Q subspaces leads to the decomposition of the T matrix into background and discrete components; the latter is often referred to as the resonant term, but this terminology could be misleading in the context of positron-molecule scattering. The discrete state contribution to the vibrational excitation T matrix is given by [15]

$$T^d_{\nu_f,\nu_i}(\mathbf{k}_f,\mathbf{k}_i) = \langle \eta_{\nu_f}|U^*_{\mathbf{k}_f} \frac{1}{E - T_N - V_{\mathrm{opt}}(E-H_N)} U_{\mathbf{k}_i}|\eta_{\nu_i}\rangle, \tag{13}$$

where the entry $(U_{\mathbf{k}_i})$ and exit $(U^*_{\mathbf{k}_f})$ amplitudes account for the electronic discrete-continuum coupling,

$$U_{\mathbf{k}} = \langle\phi_d|H_{\mathrm{ele}}|\phi_{\mathbf{k}}\rangle, \tag{14}$$

and V_{opt} is the complex potential surface of the positron-molecule transient. Though positron scattering is not of central interest in the present work, Eq. (13) unveils important aspects of the transient dynamics. The electronic capture of the positron (amplitude $U_{\mathbf{k}_i}$) launches the nuclei, initially in the vibrational eigenstate $|\eta_{\nu_i}\rangle$, onto the complex potential surface V_{opt}. The positron eventually decays to the continuum (amplitude $U^*_{\mathbf{k}_f}$), leaving the molecule in the vibrational eigenstate $|\eta_{\nu_f}\rangle$. The complex potential is given by

$$V_{\text{opt}}(\mathbf{R},E-H_N)=V_0(\mathbf{R})+\epsilon_d(\mathbf{R})+\Delta(\mathbf{R},E-H_N)-\frac{i}{2}\Gamma(\mathbf{R},E-H_N), \tag{15}$$

where $\mathbf{R}$ collectively denotes the vibrational coordinates and one should notice the operator H_N is the target's vibrational Hamiltonian

$$H_N=T_N+V_0(\mathbf{R}). \tag{16}$$

Positron attachment modifies the target ground-state PES (V_0) giving rise to the potential-energy shift

$$\epsilon_d(\mathbf{R})=\langle\phi_d|H_{\text{ele}}|\phi_d\rangle-V_0(\mathbf{R}), \tag{17}$$

where integration over electron-positron coordinates is implied. The coupling to the continuum is described by the complex, energy-dependent, and nonlocal operator whose real and imaginary parts are given by

$$\Delta(\mathbf{R},E-H_N)=\frac{1}{2\pi}\mathrm{P}\int dE'\frac{\Gamma(\mathbf{R},E'-H_N)}{E-E'} \tag{18}$$

and

$$\Gamma(\mathbf{R},E-H_N)=2\pi\int kdk\int d\hat{k}U_{\mathbf{k}}^*\delta\left(E-H_N-\frac{k^2}{2}\right)U_{\mathbf{k}}, \tag{19}$$

respectively, where the Cauchy principal value is indicated in Eq. (18). Both the level shift (Δ) and width (Γ) operators have nonlocal dependences on the nuclear coordinates (through the vibrational Hamiltonian H_N) and on the positron incident energy (off-shell integration). This poses severe difficulties for the treatment of large systems with many vibrational modes, though the judicious approximations discussed below allow for meaningful inexpensive computations. Without these simplifications, even the transformation to the time domain would be difficult, since the energy dependence of the complex potential implies non-Markovian dynamics [15,24].

Finally, a few fundamental approximations, other than the BO assumption, should be made explicit. Since we are interested in low-energy collisions, the positronium formation and electronic excitation channels may be safely neglected. The annihilation width is also assumed much smaller than the elastic and vibrationally inelastic-scattering widths [14], $\Gamma^{\text{anh}}\ll\Gamma^{\text{sct}}$, and hence omitted in the following discussion.

B. Annihilation parameter

The FPO decomposition of the scattering wave function, $|\Psi_{\mathbf{k}_i}^{(+)}\rangle=|\Psi_P\rangle+|\Psi_Q\rangle$, leads to the following expression for the angle- and energy-dependent annihilation parameter:

$$Z_{\text{eff}}(\mathbf{k}_i)=\frac{(2\pi)^3}{k_i}\langle\Psi_{\mathbf{k}_i}^{(+)}|\sum_{j=1}^{Z}\delta(\mathbf{r}_j-\mathbf{r}_p)|\Psi_{\mathbf{k}_i}^{(+)}\rangle$$
$$=\frac{(2\pi)^3}{k_i}\left\{\langle\Psi_Q|\sum_{j=1}^{Z}\delta(\mathbf{r}_j-\mathbf{r}_p)|\Psi_Q\rangle+\langle\Psi_P|\sum_{j=1}^{Z}\delta(\mathbf{r}_j-\mathbf{r}_p)\times|\Psi_P\rangle+2\,\mathrm{Re}\left[\langle\Psi_Q|\sum_{j=1}^{Z}\delta(\mathbf{r}_j-\mathbf{r}_p)|\Psi_P\rangle\right]\right\}. \tag{20}$$

A positron in the continuum (P space) is expected to have a very small density in the vicinity of the target and to be weakly coupled to nuclear motion. As a consequence, the contributions of the PP and QP terms in Eq. (20) should be negligible with respect to the QQ term that accounts for the attached positron. Hence, as in Sec. II, we shall only consider that annihilation occurs in the discrete state. With the help of Eqs. (10)–(12), (14), and (17), the Q component of the wave function may be written as

$$|\Psi_Q\rangle=|\phi_d\rangle|\xi_d\rangle=|\phi_d\rangle\frac{1}{E-T_N-V_{\text{opt}}}U_{\mathbf{k}_i}|\eta_0\rangle, \tag{21}$$

where $Q^2=Q$ and $V_{\text{opt}}=\langle\phi_d|(QH_{\text{ele}}Q+QH_{\text{ele}}PG_{PP}^{(+)}PH_{\text{ele}}Q)|\phi_d\rangle$ [18] have been employed, such that

$$Z_{\text{eff}}(\mathbf{k}_i)=\frac{(2\pi)^3}{k_i}\langle\eta_0|U_{\mathbf{k}_i}^*\frac{1}{[E-T_N-V_{\text{opt}}]^\dagger}\rho_d\times\frac{1}{[E-T_N-V_{\text{opt}}]}U_{\mathbf{k}_i}|\eta_0\rangle, \tag{22}$$

with

$$\rho_d=\langle\phi_d|\sum_{j=1}^{Z}\delta(\mathbf{r}_j-\mathbf{r}_p)|\phi_d\rangle. \tag{23}$$

In the equation above, ρ_d is the electron density at the positron, as defined in Eq. (8). Assuming that nuclear motion is weakly coupled to positron angular distributions, we may define [15],

$$\Gamma(\mathbf{R},E)=2\pi\int d\hat{\mathbf{k}}_i|U_{\mathbf{k}_i}|^2\equiv 2\pi|U_E(\mathbf{R})|^2, \tag{24}$$

to perform the angular average over $\hat{\mathbf{k}}_i$, leading to the energy-dependent annihilation parameter

$$Z_{\text{eff}}(E)=\frac{\pi}{k_i}\langle\eta_0|\Gamma^{1/2}(E)\frac{1}{[E-T_N-V_{\text{opt}}]^\dagger}\rho_d\times\frac{1}{[E-T_N-V_{\text{opt}}]}\Gamma^{1/2}(E)|\eta_0\rangle. \tag{25}$$

In the expression above, the phase of the amplitude U_E was dropped, as usual [18], on the basis of a weak dependence of the P-space wave function on the nuclear coordinates.

1. Connection with the vibrationally summed cross section

In the fixed-nuclei limit, $T_N\to 0$ and $\mathbf{R}=\mathbf{R}_0$, where $\mathbf{R}_0$ is the equilibrium geometry of the target, Eq. (25) is greatly simplified,

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i}\rho_d \frac{\Gamma(E)}{[E - \epsilon_d - \Delta(E)]^2 + \frac{1}{4}\Gamma^2(E)}, \tag{26}$$

and a simple relation with the elastic integral cross section,

$$\sigma(E) = \frac{\pi}{k_i^2} \frac{\Gamma^2(E)}{[E - \epsilon_d - \Delta(E)]^2 + \frac{1}{4}\Gamma^2(E)}, \tag{27}$$

may be easily obtained,

$$Z_{\text{eff}}(E) = \frac{k_i \rho_d}{\Gamma(E)} \sigma(E), \tag{28}$$

where the background term has been neglected in Eq. (27). Equation (28) is similar to previous results obtained in the fixed-nuclei limit for low-lying virtual or bound states [12] and it should be clear that it was derived on the assumption of negligible background (P-space) scattering. At very low energies, the width is proportional to the positron momentum (Wigner threshold law [25]), such that Z_{eff} is proportional to the cross section. An approximate expression relating the vibrationally enhanced annihilation parameter with the total (vibrationally summed) cross section,

$$\sigma_{\text{tot}}(E) = \sum_\nu \sigma_{\eta_0 \to \eta_\nu}(E) =$$

$$= \frac{\pi}{k_i^2} \sum_\nu \langle \eta_0 | \Gamma^{1/2}(E) \frac{1}{[E - T_N - V_{\text{opt}}]^\dagger} \Gamma^{1/2}(E_\nu) | \eta_\nu \rangle$$

$$\times \langle \eta_\nu | \Gamma^{1/2}(E_\nu) \frac{1}{[E - T_N - V_{\text{opt}}]} \Gamma^{1/2}(E) | \eta_0 \rangle, \tag{29}$$

may also be obtained if the operators in Eq. (25) are represented in the basis of the vibrational eigenstates of the target

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i} \sum_{\nu,\nu'} \langle \eta_0 | \Gamma^{1/2}(E) \frac{1}{[E - T_N - V_{\text{opt}}]^\dagger} | \eta_\nu \rangle \langle \eta_\nu | \rho_d | \eta_{\nu'} \rangle$$

$$\times \langle \eta_{\nu'} | \frac{1}{[E - T_N - V_{\text{opt}}]} \Gamma^{1/2}(E) | \eta_0 \rangle. \tag{30}$$

Considerable simplification may be gained if the parametric dependence of the density on the nuclear coordinates, arising from the BO discrete state $|\phi_d\rangle$, is viewed as weak,

$$\langle \eta_\nu | \rho_d | \eta_{\nu'} \rangle \simeq \rho_d(\mathbf{R}_0) \delta_{\nu\nu'}, \tag{31}$$

with a similar assumption for the entry and exit widths

$$\langle \eta_\nu | \Gamma(\mathbf{R}, E) | \eta_{\nu'} \rangle \simeq \Gamma(\mathbf{R}_0, E) \delta_{\nu\nu'}. \tag{32}$$

In this case, Eqs. (29) and (30) become

$$\sigma_{\text{tot}}(E) = \frac{\pi}{k_i^2} \Gamma(E) \sum_\nu \Gamma(E_\nu) \langle \eta_0 | \frac{1}{[E - T_N - V_{\text{opt}}]^\dagger} | \eta_\nu \rangle$$

$$\times \langle \eta_\nu | \frac{1}{[E - T_N - V_{\text{opt}}]} | \eta_0 \rangle \tag{33}$$

and

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i} \rho_d \Gamma(E) \sum_\nu \langle \eta_0 | \frac{1}{[E - T_N - V_{\text{opt}}]^\dagger} | \eta_\nu \rangle$$

$$\times \langle \eta_\nu | \frac{1}{[E - T_N - V_{\text{opt}}]} | \eta_0 \rangle. \tag{34}$$

Though these expressions point out the one-to-one correspondence between resonances in the total cross section and in the annihilation parameter, state-to-state vibrational excitation cross sections can be obtained in principle, while Z_{eff} is inherently vibrationally summed. This is a relevant fact from the theoretical standpoint, since state-to-state calculations are relatively simple and could provide a way of tuning model parameters or checking the quality of *ab initio* estimates. The information obtained from state-to-state excitation cross sections for individual modes would be invaluable to undertake the very challenging task of estimating Z_{eff} for large molecules. Unfortunately, the experimental data on positron-impact vibrational excitation are scarce and limited to small polyatomics [26].

In Eq. (33), the correct threshold behavior is imposed on the vibrational excitation cross sections through the exit width $\Gamma(E_\nu)$. For moderately high positron energies ($\gtrsim 1$ eV), it would be reasonable to neglect the vibrational excitation energy with respect to the incident energy, $\Gamma(E_\nu) \simeq \Gamma(E)$, allowing for a simple approximate relation between the annihilation parameter and the total cross section

$$Z_{\text{eff}}(E) \simeq \frac{k_i \rho_d}{\Gamma(E)} \sigma_{\text{tot}}(E). \tag{35}$$

2. Temperature effect

Since measurements of positron annihilation in molecular gases are usually carried out at room temperature, large molecules with vibrational spacings around 10^{-2} eV could attach positrons in vibrationally excited entrance channels. Mild temperature effects have been observed for moderately large molecules [27] and these can be easily taken into account by making explicit the dependence of Z_{eff} on the initial vibrational state of the target,

$$Z_{\text{eff}}^{\nu_i}(E) = \frac{\pi}{k_i} \langle \eta_{\nu_i} | \Gamma^{1/2}(E) \frac{1}{[E - T_N - V_{\text{opt}}]^\dagger} \rho_d$$

$$\times \frac{1}{[E - T_N - V_{\text{opt}}]} \Gamma^{1/2}(E) | \eta_{\nu_i} \rangle, \tag{36}$$

and taking the appropriate average over the Boltzmann distribution at temperature T,

$$\langle Z_{\text{eff}}(E) \rangle = \frac{1}{Z} \sum_i \exp(-\varepsilon_i / kT) Z_{\text{eff}}^{\nu_i}(E), \tag{37}$$

where ε_i is the vibrational energy, k is the Boltzmann constant, and Z is the partition function.

IV. USEFUL APPROXIMATIONS

As previously mentioned, the nonlocal nature of the complex potential and the high dimensionality of the vibrational

dynamics pose severe difficulties on the straightforward application of Eq. (25). These difficulties are also present in resonant electron scattering and several ways of introducing judicious simplifications have been proposed. In the following, we briefly discuss a few working approximations that might be helpful in positron-annihilation calculations.

A. Semilocal approximation

In principle, the energy dependence of the complex potential should be taken into account in low-energy positron-molecule collisions, since nonlocal effects would be expected to play a significant role in threshold phenomena [15,28]. Though this would be the desired level of description, energy-independent potentials are much more tractable and often lead to meaningful semiquantitative results. The inherent loss of accuracy would not be a severe limitation in Z_{eff} estimates since models of vibrationally enhanced annihilation usually employ empirical parameters [14] and the vibrational resonances are much narrower than the energy resolution of state-of-the-art positron beams [5], thus blurring the fine details of these structures. To compromise between computational effort and accuracy, we resort to the semilocal (SL) approximation [24] that combines a local treatment of the complex potential,

$$\Delta(\mathbf{R},E-H_N)-\frac{i}{2}\Gamma(\mathbf{R},E-H_N)\simeq\Delta_L(\mathbf{R})-\frac{i}{2}\Gamma_L(\mathbf{R}), \tag{38}$$

with energy-dependent entry widths in the numerator of Eq. (25). This approach is very convenient since the former allows for a simple matrix representation of the complex potential (also for Markovian dynamics in the time-dependent picture) and the latter is consistent with the Wigner law [25], thus appropriately accounting for the sharp threshold behavior arising from low-lying virtual or bound states [15]. The SL approach can be obtained from a separable approximation for the entry width,

$$\Gamma(\mathbf{R},E)\simeq\frac{\Gamma(E,\mathbf{R}_0)}{\Gamma_L(\mathbf{R}_0)}\Gamma_L(\mathbf{R})\equiv\gamma(E)\Gamma_L(\mathbf{R}), \tag{39}$$

where the adimensional width $\gamma(E)$ is similar to the centrifugal barriers employed elsewhere [29] to enforce the Wigner law, leading to

$$Z_{\text{eff}}(E)=\frac{\pi}{k_i}\gamma(E)\langle\eta_0|\Gamma_L^{1/2}\frac{1}{[E-T_N-V_{\text{opt}}^L]^\dagger}\rho_d \times\frac{1}{[E-T_N-V_{\text{opt}}^L]}\Gamma_L^{1/2}|\eta_0\rangle, \tag{40}$$

with

$$V_{\text{opt}}^L(\mathbf{R})=V_0(\mathbf{R})+\epsilon_d(\mathbf{R})+\Delta_L(\mathbf{R})-\frac{i}{2}\Gamma_L(\mathbf{R}). \tag{41}$$

B. Harmonic approximation

Though the matrix representation of the local operators in Eq. (40) would be straightforward in principle, the calculation of the potential surfaces could be impractical for large molecules. Considerable simplification is introduced if the potentials of the isolated target and discrete state are assumed harmonic. This approximation is often used in models of vibrationally enhanced annihilation [14] leading to good agreement with experimental data. By defining the normal modes of the isolated target, $\mathbf{Q}=\hat{\mathbf{U}}(\mathbf{R}-\mathbf{R}_0)$, the real part of the transient potential surface in Eq. (41) may be written as

$$V_R(\mathbf{Q})=\sum_j\frac{1}{2}\mu_j\omega_j^2Q_j^2+\bar{\epsilon}_d(\mathbf{Q}), \tag{42}$$

where ω_j and μ_j are frequencies and reduced masses, respectively, and

$$\bar{\epsilon}_d(\mathbf{Q})=\epsilon_d(\mathbf{Q})+\Delta_L(\mathbf{Q}). \tag{43}$$

If the difference between the potential surfaces of the target and the transient is not large, as expected for the diffuse positron-molecule compounds, the real energy shift may be Taylor expanded up to second order,

$$\bar{\epsilon}_d(\mathbf{Q})=\bar{\epsilon}_d(\mathbf{0})+\nabla\bar{\epsilon}_d(\mathbf{0})\cdot\mathbf{Q}+\frac{1}{2}\mathbf{Q}\cdot\nabla^2\bar{\epsilon}_d(\mathbf{0})\cdot\mathbf{Q}, \tag{44}$$

and the vibrational Hamiltonian of the transient will thus be given by a set of forced harmonic oscillators with bilinear couplings,

$$T_N+V_{\text{opt}}^L=\bar{\epsilon}_{d0}+\sum_j\frac{P_j^2}{2\mu_j}+\frac{1}{2}\mu_j\omega_j^2Q_j^2-\mathcal{F}_jQ_j+\frac{1}{2}\sum_{i\neq j}\mathcal{K}_{ij}Q_iQ_j -\frac{i}{2}\Gamma_L(\mathbf{Q}), \tag{45}$$

where $\bar{\epsilon}_{d0}=\bar{\epsilon}_d(\mathbf{0})$ is the vertical shift at the equilibrium geometry of the target, $\mathcal{F}_j=-\partial_j\bar{\epsilon}_d$, and $\mathcal{K}_{ij}=\partial_{ij}^2\bar{\epsilon}_d$. Equations (44) and (45) provide great physical insight into the transient dynamics. If, to a first approximation, the vibrational couplings of the width $\Gamma_L(\mathbf{Q})$ are neglected, vibrationally excited resonances will be coupled through the real potential-energy shift $\bar{\epsilon}_d$, i.e., the difference between the real part of the transient potential surface and the target potential surface. Up to zeroth order, they only differ by the constant vertical shift $\bar{\epsilon}_{d0}$ and a single resonance (vibrational ground state) will be found. The first-order term accounts for the effect of positron attachment on the individual vibrational modes, essentially coupling single-mode excitations, while the second-order term allows for two-mode excitations and hence for intermode couplings (vibrational energy redistribution). The outcome of isotope effects (e.g., deuteration in C-H stretch modes) is also very clear. The parameters related to positron attachment, namely, $\bar{\epsilon}_{d0}$, $\mathcal{F}_j$, and $\mathcal{K}_{ij}$, are essentially unaffected by different isotopes, since they arise from correlation-polarization forces. The frequencies and reduced masses, on the other hand, might change, thus shifting the resonance positions according to $\omega\propto\mu^{-1/2}$.

C. Time-dependent approach

For large molecules with many vibrational modes, the matrix representation and inversion of the operators in the de-

nominator of Eq. (40) can be time consuming even for harmonic potentials. The time domain would be more convenient to deal with the high dimensionality of the problem, especially with a local treatment of the complex potential. In the SL approximation [24], the time evolution of the nuclear wave packet is described by the local Schrödinger equation,

$$i\frac{\partial}{\partial t}\xi_d(\mathbf{R},t) = \left[T_N + V_0(\mathbf{R}) + \bar{\epsilon}_d(\mathbf{R}) - \frac{i}{2}\Gamma_L(\mathbf{R})\right]\xi_d(\mathbf{R},t), \quad (46)$$

with the initial condition

$$\xi_d(\mathbf{R},t\to 0^+) = \sqrt{\frac{\Gamma(\mathbf{R},E)}{2\pi}}\eta_0(\mathbf{R}) \simeq \gamma^{1/2}(E)\sqrt{\frac{\Gamma_L(\mathbf{R})}{2\pi}}\eta_0(\mathbf{R}). \quad (47)$$

This separable form of the entry width allows for the time propagation of an strictly energy-independent wave packet $\tilde{\xi}_d(\mathbf{R},t)$ defined by

$$\xi_d(\mathbf{R},t) = \gamma^{1/2}(E)\tilde{\xi}_d(\mathbf{R},t) \quad (48)$$

and

$$\tilde{\xi}_d(\mathbf{R},t\to 0^+) = \sqrt{\frac{\Gamma_L(\mathbf{R})}{2\pi}}\eta_0(\mathbf{R}). \quad (49)$$

By transforming the wave packet to the energy domain,

$$\langle \mathbf{R}|\tilde{\xi}_d(E)\rangle = -i\int_0^\infty dt e^{iEt}\int d\mathbf{R}' K(\mathbf{R},t|\mathbf{R}',0)\tilde{\xi}_d(\mathbf{R}',t=0), \quad (50)$$

where $K(\mathbf{R},t|\mathbf{R}',0)$ is the Feynman propagator of Eq. (46), Z_{eff} estimates may be readily obtained

$$Z_{\text{eff}}(E) = \frac{\pi}{k_i}\gamma(E)\langle\tilde{\xi}_d(E)|\rho_d|\tilde{\xi}_d(E)\rangle. \quad (51)$$

If the vibrational Hamiltonian of the transient is given by a set of coupled harmonic oscillators, as in Eq. (45), advantage may be taken from well-known time propagation techniques. Similar approximations are routinely employed, for instance, in quantum dissipation [30] and chemical reaction dynamics [31,32]. In particular, the time-dependent self-consistent field approach [33] leads to a set of single-mode effective dynamical equations that incorporate mean-field intermode couplings. The propagator of these effective equations is known in closed form [34] and may allow for very efficient implementations. Though it is exciting that chemical reaction techniques could be useful to describe energy-resolved positron annihilation, we postpone the implementation of more elaborate models and discuss simple semiempirical calculations in the next section.

V. MODEL CALCULATIONS

We present a simple model, based on the preceding discussion, and apply it to acetylene and ethylene, since the choice of model parameters for these molecules can be guided by previous studies of positron scattering. The simplest description of the complex potential is obtained from energy- and position-independent widths,

$$\Gamma_L(\mathbf{R}) \simeq \Gamma_L(\mathbf{R}_0) \equiv \Gamma_L, \quad (52)$$

and from linear potential-energy shifts,

$$\bar{\epsilon}_d(\mathbf{Q}) = \bar{\epsilon}_d(\mathbf{0}) + \nabla\bar{\epsilon}_d(\mathbf{0})\cdot\mathbf{Q}, \quad (53)$$

where the harmonic approximation has been assumed. The expression above neglects intermode couplings, giving rise to a separable dynamical equation for the positron-molecule compound,

$$i\frac{\partial}{\partial t}\tilde{\xi}_d(\mathbf{Q},t) = \left[\bar{\epsilon}_{d0} + \sum_j\left(\frac{P_j^2}{2\mu_j} + \frac{1}{2}\mu_j\omega_j^2Q_j^2 - \mathcal{F}_jQ_j\right) - \frac{i}{2}\Gamma_L\right]\tilde{\xi}_d(\mathbf{Q},t), \quad (54)$$

and hence to

$$Z_{\text{eff}} = \frac{\pi}{k_i}\rho_d\Gamma(E)\sum_{\boldsymbol{\nu}} g_{\boldsymbol{\nu}}\frac{|c_{\boldsymbol{\nu},0}|^2}{(E-\bar{\epsilon}_{d0}-\varepsilon_{\boldsymbol{\nu}})^2 + (\Gamma_L/2)^2}, \quad (55)$$

with the help of Eqs. (31), (50), and (51). The transient single-mode spectra,

$$\left(\frac{P_j^2}{2\mu_j} + \frac{1}{2}\mu_j\omega_j^2Q_j^2 - \mathcal{F}_jQ_j\right)|\chi_{\nu j}\rangle = \varepsilon_{\nu j}|\chi_{\nu j}\rangle, \quad (56)$$

define the multimode resonance energies $\varepsilon_{\boldsymbol{\nu}}=\varepsilon_{\nu_1}+\cdots+\varepsilon_{\nu_M}$, where M is the number of vibrational modes, the degeneracies $g_{\boldsymbol{\nu}}\equiv g_{\nu_1\cdots\nu_M}$, and the Frank-Condon overlaps $c_{\boldsymbol{\nu},\mathbf{0}}=\langle\chi_{\nu_1}|0_{\nu_1}\rangle\cdots\langle\chi_{\nu_M}|0_{\nu_M}\rangle$, where 0_j denotes the ground state of the jth vibrational mode of the isolated target (entrance channel).

In Eq. (55), the parameters $\bar{\epsilon}_{d,0}$, Γ_L, and $\Gamma(E)$ may be easily obtained from scattering calculations (see below). For low-lying positron-molecule bound states, the density is usually described as $\rho_d=(F/2\pi)\kappa_0$, where $F=0.66$ and $\kappa_0^2/2$ is the binding energy [14]. We follow the same prescription, assuming its validity for either bound or virtual states in the limit $|\kappa_0|\to 0$, i.e., we expect very diffuse virtual and bound states to have similar electron densities at the positron. The essential physics of the model resides on the Frank-Condon factors that account for the relative strengths of the vibrational resonances and these can be readily obtained as functions of the linear forces $\mathcal{F}_j$, in view of Eq. (56). A measure of these strengths is provided by the ratio of the energy correction arising from the linear forces to the vibrational spacings of the target

$$\frac{(\mathcal{F}_j^2/2\mu_j\omega_j^2)}{\omega_j} = \frac{\mathcal{F}_j^2}{2\mu_j\omega_j^3} \equiv \zeta. \quad (57)$$

To keep the number of empirical model parameters as small as possible, we employ the same adimensional strength parameter ζ_{ir} for all infrared (ir) active modes, and arbitrarily set $\zeta=(\zeta_{\text{ir}}/10)$ for all ir inactive modes, based on the experimental evidence that resonant annihilation is much stronger for ir active modes [5]. The model thus has a single empirical

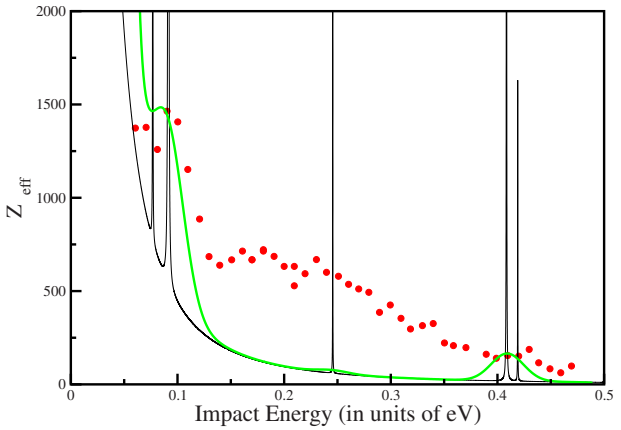

FIG. 3. (Color online) Annihilation parameter for C_2H_2. Red circles: experimental data of [11]; thin black curve: calculated Z_{eff}; thick green curve: convoluted Z_{eff}.

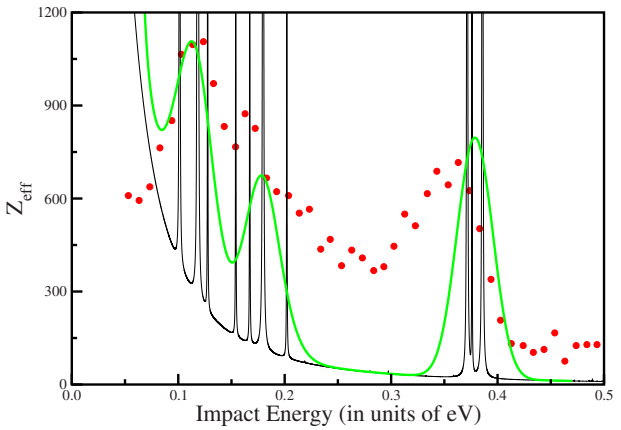

FIG. 4. (Color online) Annihilation parameter for C_2H_4. Red circles: experimental data of [11]; thin black curve: calculated Z_{eff}; thick green curve: convoluted Z_{eff}.

parameter (ζ_{ir}), though with different linear coupling forces ($\mathcal{F}_j$) among ir-active and -inactive modes, in view of Eq. (57). In practice, ζ_{ir} is chosen to provide the best agreement with experimental data and the Frank-Condon factors arising from individual $\mathcal{F}_j$ values give rise to the relative resonance strengths in Eq. (55).

Results

Recent studies of positron scattering by acetylene [10] guided the choice of parameters for this system. The low-lying virtual state at the equilibrium geometry of the target lead us to set $\bar{\epsilon}_{d0}=1$ meV and $\Gamma_L=2\times10^{-4}$ eV was chosen based on the widths of $0\rightarrow1$ resonances for C–C and C–H stretch modes. The energy dependence of $\Gamma(E)$ was obtained by fitting a model width to *ab initio* *s*-wave phase shifts, as described elsewhere [16], and the harmonic frequencies and reduced masses were taken from the NIST database [35]. The present calculations were convoluted over a 35 meV (full width at half maximum) Gaussian profile to approximately account for the experimental resolution [11] and the results obtained for $\zeta_{\mathrm{ir}}=5.5\times10^{-5}$ are shown in Fig. 3. The local approximation for the complex potential (V_{opt}^{L}) neglects its significant energy dependence [16] and this limitation is particularly evident for the $\nu=0$ resonance in view of its large Franck-Condon factor (~1). Nevertheless, the strongest experimental peaks are fairly well described by this extremely simple model.

Though ethylene has a slightly higher-lying virtual state at the equilibrium geometry than acetylene [9], we employed the same parameters ($\bar{\epsilon}_{d0}$, $\Gamma(E)$, and Γ_L) described above for this molecule. In practice, the model is relatively insensitive to the values of these parameters, since small variations are compensated by slightly different ζ_{ir} values. The results for ethylene are shown in Fig. 4 ($\zeta_{\mathrm{ir}}=1.7\times10^{-4}$) and reasonable agreement with the experimental data of Gilbert *et al.* [11] is found again.

Though our results could be improved in several different ways, e.g., by using different strength parameters (ζ) or different local widths (Γ_L) for individual modes, taking intermodes couplings into account, improving the description of the complex potential, or even including the background contribution, we believe this simplest approach already captures the essentials of annihilation dynamics. Because overtones and combination vibrations are very weakly coupled through the linear forces $\mathcal{F}_j$, this model essentially accounts for $0\rightarrow1$ excitations, fairly describing these resonances. Finally, we observe that overtones and combination vibrations are found in the energy range where agreement with experimental data is poor, suggesting that intermode couplings could play a relevant role.

VI. CONCLUSIONS

We proposed a theory of vibrationally enhanced positron annihilation on molecules based on the Feshbach projection operator formalism. The vibrational resonances responsible for very high annihilation rates arise from the electronic capture of the positron in either virtual or bound states, as opposed to direct positron-impact excitation. An approximate relation between the annihilation parameter and the vibrationally summed cross section was presented, as well as a hierarchy of approximations that may allow for elaborate model calculations. We also discussed how important aspects of the annihilation process are taken into account in the present theory, such as isotope effects, vibrational energy redistribution, and relative strengths among vibrational resonances. For completeness, simple model calculations for acetylene and ethylene were presented. Despite the stringent approximations employed in these semiempirical calculations, fair agreement with experimental data [11] was obtained in the vicinity of $0\rightarrow1$ thresholds, as expected. Improved models will be discussed in future publications.

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