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Positron interactions with molecules

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Abstract. In this work, we report elastic integral cross sections for low energy positron scattering by carbon monoxide and model calculations for vibrationally enhanced positron annihilation on molecules. The former studies employed the Schwinger Multichannel method in the static plus polarization approximation with two different basis sets to access numerical convergence. In the annihilation studies, the role of multimode vibrational couplings was surveyed with the help of an analytically solvable model based on the Feshbach projection operator formalism.

1. Introduction

In recent years, experimental advances have allowed for several scientific and technological applications of positron-matter interactions (see [1] for a review), such as materials characterization [2], positron emission tomography [3] and in the study of anti-hydrogen [4] and positronium molecules [5]. However, there are still open questions on fundamental positron interactions. Even for the most basic positron-molecule processes, agreement among the available theories and experimental data is far from satisfactory.

In studies of positron-molecule scattering, for instance, though some accordance is found for integral cross sections (ICS) [1], forward angle scattering effects might significantly impact total cross section experiments [6, 7]. In addition, the low intensity of positron beams poses even more severe difficulties for differential cross section (DCS) measurements. Though the comparison between theory and early relative DCS data[8] was encouraging [9], a big discrepancy is found between recent absolute DCS results and theory [10, 11]. On the theoretical side, the difficulties arise from the repulsive static positron-molecule interaction, which imposes a very thorough description of target polarization, and from the role short-range positron-electron correlation.

The description of vibrationally enhanced positron annihilation on molecules, a field of intense activity [12], is even more challenging for theoreticians. The positron annihilation rate in a molecular gas (λ) can be obtained from the well-known relation

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

where r_0 is the classical electron radius, c is the velocity of light, n is the gas density, and the annihilation parameter, averaged over positron incident directions, is given by

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

where Z is the number of target electrons $\Psi_{k_i}^{(+)}$ is the scattering wave function, and k_i is the magnitude of the positron incident wave vector. In addition to the difficulties related to correlation- polarization effects mentioned above, the positron couplings to nuclear degrees of freedom that dramatically affect Z_{eff} [12] values are not well understood. In view of these facts, *ab initio* computational simulations have provided limited information on this process [13, 14], such that much of the current understanding relies on semi-empirical theories [15, 16].

Our group has been undertaking efforts in two directions, namely *ab initio* simulations of fixed-nuclei positron-molecule scattering and theories of resonant positron annihilation [14, 16, 17] based on the Feshbach projection operator (FPO) formalism [18]. In this work, (i) we report low energy ICS for elastic positron scattering by carbon monoxide, as a first step towards more the challenging elastic DCS and vibrationally inelastic calculations; and (ii) we discuss essential aspects of multimode effects in resonant annihilation, with the help of the FPO approach. The paper is organized as follows. In the next Section, we outline the SMC method and the FPO theory; the results are discussed in Secs. 3 and 4, and the conclusions are given in Sec. 5.

2. Methods

2.1. Fixed-nuclei scattering calculations

Elastic ICS were computed with the Schwinger Multichannel method (SMC) in the fixed nuclei approximation. Details of the formulation are given elsewhere [19, 10]. The working expression for the scattering amplitude is given by

$$[f_{i,f}] = -\frac{1}{2\pi} \sum_{\nu,\mu} \langle S_{\vec{k}_i} | V | \chi_\nu \rangle (d^{-1})_{\nu\mu} \langle \chi_\mu | V | S_{\vec{k}_f} \rangle, \quad (3)$$

with

$$d_{\mu\nu} = \langle \chi_\mu | A^{(+)} | \chi_\nu \rangle, \quad (4)$$

and

$$A^{(+)} = PVP + Q\hat{H}Q - VG_P^{(+)}V. \quad (5)$$

In the expressions above, $S_{\vec{k}}$ is an eigenstate of the free Hamiltonian, given by the product of a plane wave (positron) and the electronic ground state of the target; V is the positron-target scattering potential; χ_ν is a configuration state function (product of a target electronic state by a scattering orbital); $\hat{H} = E - H$ is the collision energy minus the scattering Hamiltonian; P is a projection operator onto the open (energy accessible) electronic states of the target; $G_P^{(+)}$ is the free Green's function projected onto P space and $Q = (1 - P)$ projects on the closed-channel space.

Since we are only interested in elastic collisions, we set $P = |\Phi_0\rangle\langle\Phi_0|$, where Φ_0 is the target electronic ground state, obtained at the restricted Hartree-Fock level. The SMC approach accounts for polarization effects in an *ab initio* fashion, through single virtual excitations of the target.

2.2. Resonant positron annihilation

In a previous paper [14], we developed a theory of positron annihilation based the Feshbach projection operator formalism [18]. This approach describes the capture of the positron into a discrete state $|\phi_d\rangle$ coupled to a dense scattering set, such that virtual or bound e^+ -molecule states can be accounted for. The discrete state is assumed parametrically dependent on the nuclear coordinates and orthogonal to the set of continuum states $\{|\phi_k\rangle\}$. The scattering wave function can thus be decomposed as $|\Psi_{\mathbf{k}_i}^{(+)}\rangle = \mathcal{P}|\Psi_{\mathbf{k}_i}^{(+)}\rangle + \mathcal{Q}|\Psi_{\mathbf{k}_i}^{(+)}\rangle$, where $\mathcal{Q} = |\phi_d\rangle\langle\phi_d|$ and $\mathcal{P} = (1 - \mathcal{Q})$. The annihilation parameter is obtained as (see details in [14]):

$$Z_{\text{eff}} = \frac{\pi}{k_i} \langle\eta_i| \Gamma^{1/2}(E) \frac{1}{[E - K - V_{\text{opt}}]^\dagger} \rho_d \frac{1}{[E - K - V_{\text{opt}}]} \Gamma^{1/2}(E) |\eta_i\rangle, \quad (6)$$

where

$$\rho_d = \langle\phi_d| \sum_{\alpha=1}^Z \delta(\mathbf{r}_p - \mathbf{r}_\alpha) |\phi_d\rangle \quad (7)$$

is the electronic density at the positron (\mathbf{r}_p and \mathbf{r}_α are positron and electron coordinates, respectively), η_i is the initial vibrational eigenstate of the target, K is the nuclear kinetic energy, $\Gamma(E)$ is the capture width, and V_{opt} is the complex, non-local and energy-dependent potential of the positron-molecule transient [14, 16, 18]. Positron attachment, a fast process in the time scale of molecular vibrations, launches the nuclei (originally on the potential energy surface (PES) of the target ground state) onto the complex potential of the e^+ -molecule compound. As the vibrational state will no longer be stationary, the capture process (driven either by short-ranged correlation-polarization effects or long-ranged dipole interactions) provides an efficient mechanism for energy transfer into vibrational degrees of freedom.

3. Positron scattering by carbon monoxide

We describe the target at the Hartree-Fock (HF) level using a 13s8p3d cartesian gaussian basis set. The calculated dipole moment (-0.128 D) is not in good agreement with the experimental value ($+0.044$ D) as expected for the HF approximation [20]. The scattering wave function was augmented with an additional 2s3p2d set on the molecular center of mass (CM).

Our calculations were performed at the static plus polarization approximation for energies ranging from 0.030 to 7.0 eV, below the positronium (Ps) formation threshold of 7.2 eV [21] (the Ps formation channel is not accounted for in our calculations). Polarization effects were included through virtual single excitations into modified virtual orbitals. The total number of configurations with this basis set was 34,101 (Basis 1). To access the convergence of the variational space, we also included a diffuse f-type function (exponent $0.002 a_0^{-2}$) on the CM, thus obtaining 42,861 configurations (Basis 2).

In Figure 1, we show ICS results obtained with Basis 1 and 2, along with the calculations of Gianturco *et al.* [22], Arretche *et al.* [11] and the experimental data of Kwan *et al.* [23], and Sueoka and Hamada [24]. Though the theories do not agree around 1.0–3.0 eV, they provide lower and upper bounds for the experimental data below 5 eV. At higher energies, albeit below the Ps formation threshold, the measurements lie above the theoretical curves. Since the experimental data were obtained with a positron beam with full width at half maximum (FWHM) of approximately 2.0 eV, this difference could be a signature of Ps formation.

4. Model for positron annihilation on molecules

The straightforward application of Eq. (6) is very difficult since the complex potential is non-local and energy-dependent. A model based on the well known local approximation was developed, as described elsewhere [14, 17], and could account for the essential physics of vibrationally enhanced

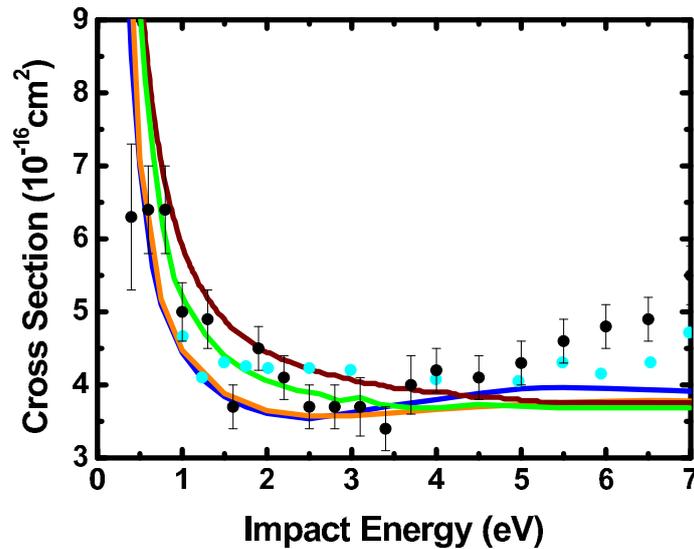


Figure 1. Integral cross section for positron-CO scattering. Blue curve: present results for basis 1; orange curve: present results for basis 2; brown curve: results from [22]; green curve: data of [11]; blue circles: experiment of [23]; black circles: measurement of [24].

annihilation. The proposed mechanism involves the electronic capture of the positron in bound or virtual states, with subsequent energy transfer into vibrational degrees of freedom. Long-lived transients allow for constructive interference at the vibrational levels of the compound, giving rise to sharp vibrational resonances.

The underlying dynamical picture can be understood on the basis of the following model. The local approximation resorts to the very useful concept of a complex PES, $V_{\text{opt}} = V_0 + \Delta V - (i/2)\Gamma$, where V_0 is the target PES, ΔV is the shift arising from positron attachment and the width Γ accounts for the finite lifetime of the transient. The nuclear dynamics on this complex potential is governed by the time-dependent Schrödinger equation,

$$i \frac{\partial}{\partial t} |\xi(t)\rangle = [K + V_{\text{opt}}] |\xi(t)\rangle, \quad (8)$$

where ξ is the nuclear wave packet subjected to the initial condition,

$$|\xi(t = 0^+)\rangle = \left[\frac{\Gamma}{2\pi} \right]^{1/2} |\eta_{\nu_i}\rangle, \quad (9)$$

and $|\eta_{\nu_i}\rangle$ is the initial vibrational eigenstate of the isolated target. Equation 8 can be solved with the help of the vibrational spectrum of the compound Hamiltonian $(K + V_0 + \Delta V)|\chi_{\nu}\rangle = \epsilon_{\nu}|\chi_{\nu}\rangle$, such that, after transformation to the energy domain, the final expression for Z_{eff} is given by

$$Z_{\text{eff}} = \frac{\pi}{k_i} \rho_d \sum_{\nu} |c_{\nu 0}|^2 \frac{\Gamma}{(E - \epsilon_{\nu}^2 + \Gamma^2/4)}. \quad (10)$$

In the expressions above, $\epsilon_{\nu} = \epsilon_{\nu 1} + \epsilon_{\nu 2} + \dots + \epsilon_{\nu M}$ is the multimode vibrational energy, where M is the total number of vibrational modes, and $c_{\nu 0} = \langle \chi_{\nu 1} | 0_{\nu 1} \rangle \dots \langle \chi_{\nu M} | 0_{\nu M} \rangle$ are the Frank-Condon (FC) overlaps that arise from the target vibrational ground state $|0_{\nu 1} \dots 0_{\nu M}\rangle$ and the compound vibrational states $|\chi_{\nu 1} \dots \chi_{\nu M}\rangle$. These FC factors account for the relative coupling strengths among the vibrational modes, an important fact as the experimental data point out that infrared (IR) active modes give rise to stronger annihilation peaks [12]. Since the time

evolution of the wave packet takes place on the transient potential, transformation to the energy domain gives rise to resonant peaks on the vibrational eigenstates of $(K + V_0 + \Delta V)$, according to Equation 10.

A solvable model can be obtained as follows. (i) The target vibrational Hamiltonian $H_N = (K + V_0)$ is assumed harmonic, $2V_0(\mathbf{Q}) = \sum_j \mu_j \omega_j^2 Q_j^2$, and (ii) any couplings arising from the width Γ are neglected. As a result, the annihilation dynamics, *i.e.* the vibrational modes coupled to positron attachment, will be given by the potential energy shift ΔV . In other words, the initial state $|0_{\nu_1} \cdots 0_{\nu_M}\rangle$ will evolve into a non-stationary wave packet upon positron capture as the PES suddenly changes from V_0 to $(V_0 + \Delta V)$. To point out how this potential energy shift can give rise to annihilation spectra, we consider two different coupling schemes. (I) The potential energy perturbation due to positron attachment is viewed as small, such that ΔV can be Taylor series expanded up to first order, $\Delta V = -\sum_i F_i Q_i$, where the zero-th order term was set to zero (this constant would only uniformly shift the resonance peaks). (II) A stronger coupling to positron attachment could excite overtones and two-mode (in general multimode) resonances according to $\Delta V = -\sum_i F_i Q_i + \sum_{ij} K_{ij} Q_i Q_j$. The energy dependence of Z_{eff} obtained from the schemes I and II described above is shown in Fig. 2. In these plots, we considered four vibrational modes, with frequencies $\hbar\omega_1 = 0.10$ eV, $\hbar\omega_2 = 0.15$ eV, $\hbar\omega_3 = 0.20$ eV and $\hbar\omega_4 = 0.25$ eV. Modes 1 and 3 were assumed strongly coupled to positron attachment, with linear couplings (F_i) exceeding those of modes 2 and 4 by one order of magnitude. In scheme I (red lines in Fig. 2), the neglect of two-mode couplings essentially allows for $\nu = 1$ resonances, with relative intensities given by F_i . In scheme II (blue lines in Fig. 2), we employed the same value for all coupling constants K_{ij} for simplicity. The annihilation spectrum is much richer as it comprises overtones (arising from the curvature corrections, K_{ii}) and two-mode couplings (arising from the off-diagonal terms, K_{ij}).

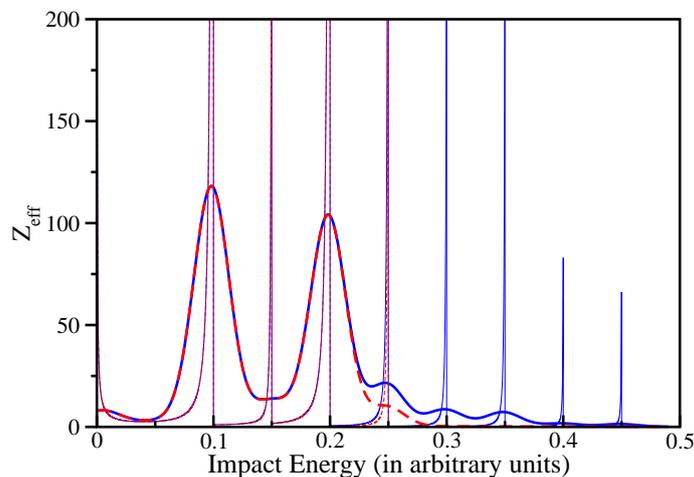


Figure 2. Annihilation parameter for a *toy* system. The thin lines with sharp structures are the present calculations: red dashed line considers only single mode couplings, blue line takes into account also the multimode vibrational coupling. The smooth thick lines (with the same color scheme) are convolutions of these results over a Gaussian profile with 35 meV full width at half maximum.

Finally, we mention that the potential energy shift ΔV accounts for distortions of the compound state PES with respect to V_0 . As these distortions can arise from correlation-polarization effects, they provide a universal mechanism for the coupling of both IR active

and inactive modes. Nevertheless, the static long-ranged dipole interaction (that only couples IR active modes) can play an important role.

In this work, we resorted to the local approximation, even though the energy dependence of the complex potential should be important at very low positron energies. However, to the best of our knowledge, all existing theories of this matter treat this problem with the use of empirical parameters [14, 15]. Further, since the positron beam in the experiment has a wider resolution than the resonances, we do not consider this approximation to qualitatively compromise our results, since fine details of these structures can not be seen.

5. Conclusions

We present results for low-energy integral cross sections for positron-CO scattering and model calculations for resonant positron annihilation. Our ICS results show reasonable agreement with the available theoretical and experimental data. Through our model calculation, it was possible to show how the FPO formalism can account for the underlying dynamics of vibrationally enhanced annihilation in positron-molecule scattering.

Acknowledgments

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References

- [1] Surko C M, Gribakin G F and Buckman S J 2005 *J. Phys. B* **38** R567
- [2] Schultz P J and Lynn K. G. 1998 *Rev. Mod. Phys.* **60** 701
- [3] Wahl R L and Buchanan J W (eds) 2002 *Principles and Practice of Positron Emission Tomography* Philadelphia, PA, Lippincott Williams and Wilkins
- [4] Amoretti M *et al.* 2002 *Nature* **419** 456; Gabrielse G 2008 *et al. Phys. Rev. Lett.* **100** 113001; Andresen G B *et al.* 2010 *Nature* **468** 673
- [5] Cassidy D B and Mills A P 2007 *Nature* **449** 195; Surko C M 2007 *Nature* **449**, 153
- [6] Hamada A and Sueoka O 1994 *J. Phys. B* **27** 5055
- [7] Sullivan J P *et al.* 2011 *J. Phys. B* **44** 035201
- [8] Przybyla D A, Addo-Asah W, Kauppila W E, Kwan C K and Stein T S 1999 *Phys. Rev. A* **60** 359
- [9] see, for example, Sanchez S D, Arretche F and Lima M A P 2008 *Phys. Rev. A* **77** 054703; Zecca A, Chiari L, Sarkar A, Lima M A P, Bettega M H F, Nixon K L and Brunger M J 2008, *Phys. Rev. A* **78** 042707; and references therein.
- [10] Sanchez S d'A and Lima M A P 2008, *Nucl. Inst. and Meth. in Phys. Res. B* **266**, 447
- [11] Arretche F, Mazon K, Michelin S, Fujimoto M, Iga I and Lee M -T 2008, *Nucl. Instr. and Meth. B* **266**, 441
- [12] Gribakin G F, Young J A and Surko C M 2010, *Rev. Mod. Phys.* **82**, 2557
- [13] Nishimura T and Gianturco F A 2005 *Phys. Rev. A* **72** 022706
- [14] Sanchez S d'A, Lima M A P and Varella M T do N 2009 *Phys. Rev. A* **80** 052710
- [15] Gribakin G F and Lee C M R 2006 *Phys. Rev. Lett.* **97** 193201
- [16] Varella M T do N and Lima M A P 2007 *Phys. Rev. A* **76** 052701; Varella M T do N *et al.* 2008 *Nucl. Instrum. and Meth. B* **266** 435
- [17] Sanchez S d'A, Lima M A P and Varella M T do N 2011 *Phys. Rev. Lett.* **107** 103201
- [18] O'Malley T F 1966 *Phys. Rev.* **150** 14; Dubé L and Herzenberg A 1979 *Phys. Rev. A* **20** 194; Hazi A U *et al.* 1981 *Phys. Rev. A* **23** 1089; Domcke W 1991 *Phys. Rep.* **208** 97
- [19] Germano J S E and Lima M A P 1993 *Phys. Rev. A* **47** 3976.
- [20] Szabo A and Ostlund N S 1989 *Modern Quantum Chemistry: introduction to advanced electronic structure theory*, Dover Publication Inc., New York
- [21] Colemann P G, Griffith T C and Heyland G R 1974 *Appl. Phys.* **4** 89
- [22] Gianturco F A Mukherjee T and Paoletti P 1997 *Phys. Rev. A* **56** 3638
- [23] Kwan Ch K *et al.* 1983 *Phys. Rev. A* **27** 1328
- [24] Sueoka O and Hamada A 1993 *J. Phys. Soc. Jpn.* **62** 2669
- [25] Young J A *et al.* 2008 *Phys. Rev. A* **77** 060702(R) Young J A and Surko C M 2008 *Phys. Rev. A* **78** 032702