Annihilation Dynamics of Positrons in Molecular Environments: Theoretical Study of Low-Energy Positron-C_2H_4 Scattering

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We present a theoretical study of low-energy positron-C_2H_4 scattering using the Schwinger multichannel method. We calculated integral cross sections and the annihilation parameter Z_{eff} for positron impact energies from 0.001 to 6 eV. We have used up to 23 112 configurations in a fully *ab initio* calculation. Our results are in excellent agreement with available experimental data. As seen experimentally, at low energies, our calculated Z_{eff} and cross sections are very large. We attribute this behavior to virtual positronium formation. [S0031-9007(96)00794-6]

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Techniques of stabilization of positron clouds for studies of annihilation rates of positrons in molecular environments have been successfully developed in these last few years [1]. In these experiments [2] it is found that for some molecular systems the positron annihilation parameter Z_{eff} is much larger than the expected classical values (proportional to Z, the number of electrons in the molecule). Surprisingly, for some molecules the rate Z_{eff}/Z gets close to 10^{+5} at thermal energies [2]. Up to date, no complete theoretical explanation has been given to this phenomena. Motivated by these experiments and by the fact that positron beams are becoming very dense and stable (allowing crossed beam experiments which may furnish differential and integral cross sections [3,4]), we have developed and implemented a Schwinger multichannel (SMC) method for positrons [5] and computer codes to evaluate Z_{eff} from the SMC wave function [6]. Our method was successfully applied to He and H_2, systems with Z_{eff}/Z equal to 2 and 7, respectively. In this Letter we present the first application of the method to a polyatomic molecule, C_2H_4, which experimental rate Z_{eff}/Z was found to be equal to 75 [2].

In the SMC method the expression for the scattering amplitude [5] is given by

$$[f(\vec{k}_f, \vec{k}_i)] = -\frac{1}{2\pi} \sum_{m,n} \langle S_{\vec{k}_f} | V | \chi_m \rangle (A^{(+)-1})_{mn} \langle \chi_n | V | S_{\vec{k}_i} \rangle,$$ (1)

where

$$A^{(+)} = Q\hat{H}Q + PVP - VG_p^{(+)}V.$$ (2)

In these equations $S_{\vec{k}_i}$ is a product of a target state and a plane wave, V is the interaction potential between the positron and the molecular target, χ_n is a $(N+1)$-particle wave function used as a variational trial function, $\hat{H}$ is

the total energy minus the full Hamiltonian of the system, N is the total number of electrons in the target, P is a projector onto the energetically open electronic states of the target and Q onto the closed states, and $G_p^{(+)}$ is the Green's function projected on this P space. The Z_{eff} parameter is related to the probability of an electron and a positron to be found in the same position [7], i.e.,

$$Z_{eff}(\vec{k}_i) = \sum_{j=1}^{N} \langle \Psi_{\vec{k}_i}^{(+)}(\vec{r}_1, \ldots, \vec{r}_N, \vec{r}_p) | \delta(\vec{r}_j - \vec{r}_p)$$
$$\times | \Psi_{\vec{k}_i}^{(+)}(\vec{r}_1, \ldots, \vec{r}_N, \vec{r}_p) \rangle.$$ (3)

To obtain this parameter for C_2H_4 we used the SMC $(N+1)$-particle scattering wave function [6],

$$|\Psi_{\vec{k}_i}^{(+)}\rangle = \sum_{m,n} |\chi_m\rangle (A^{(+)-1})_{mn} \langle \chi_n | V | S_{\vec{k}_i} \rangle.$$ (4)

In low-energy positron-molecule (or -atom) scattering polarization effects and positronium formation play very important roles. We classify the positron-molecule interactions in three different levels. (1) Static: due to proton-positron and electron-positron Coulombic potentials, assuming that the target is frozen during the collision process (all electrons are kept in their molecular orbitals). (2) Long range polarization potential: the positron creates a temporary dipole on the target by attracting the electronic molecular cloud towards itself (this is the well-known, always attractive, $1/r^4$ potential). (3) Short range polarization potential: the positron reaches the inner region of the electronic charge, loses its energy by causing virtual or real electronic excitation of the molecule (it may also participate in the formation of a temporary composite system e^+ + molecule). Electronic excitations by positron impact can be done to bound and

to continuum states of the molecule and may be related to two types of positronium formation: real and virtual. When the incoming positron has sufficient energy, it may extract one electron and take it away from the target, forming a positronium in the asymptotic region. This is the so-called real positronium formation. If the incoming positron is too slow, there is not enough energy to take the electron away from the molecular target, and in this case the positronium is virtual.

The description of the positron-molecule collision process in the SMC method is done in the following way: (1) The static approximation is obtained by defining $P = |\Phi_0\rangle\langle\Phi_0|$, where $|\Phi_0\rangle$ is the ground state of the target, Q is made equal to zero, and the set of trial functions $\{\chi_m\}$ is obtained by simple products of $|\Phi_0\rangle$ and one-particle scattering functions. (2) Short and long range polarization effects [5] are included by defining $Q = \sum_\ell |\Phi_\ell\rangle\langle\Phi_\ell|$ where $|\Phi_\ell\rangle$ are excited states of the target (only those which are energetically forbidden) and the set of trial functions $\{\chi_m\}$ is expanded from the static situation by including all simple products of $|\Phi_\ell\rangle$ and one-particle scattering functions. In the present version of the SMC method, real positronium formation (due to electronic excitations of the continuum states of the target) is not taken into account. On the other hand, all electronic excitations to bound states of the target can be included in the calculation either in the P space (if the states are energetically open) or in the Q space (if they are energetically closed). Virtual positronium formation (defined here as a positronium bounded to a molecular ion) is thus fully accounted in the method. Below real positronium formation thresholds, the main restriction of the method is due to the natural limitation in size of the trial basis set $\{\chi_m\}$.

In our procedures the target wave function is obtained by a Hartree-Fock calculation using a set of Cartesian Gaussian functions $(9s5p/4s2p)$ for the C atoms [8] incremented by s (0.03) and p (0.02) functions. For the H atoms we have used a $5s/3s$ set [9] with an additional p (0.2) function. All virtual orbitals obtained in the self-consistent-field (SCF) calculation plus a set of additional s (0.05) and p (0.085) functions placed on the center of mass of the molecule and another set at the corners of a square of side $2.6a_0$ (perpendicular to C-C bound) are used in the construction of the configuration space. We have chosen the size of the square and the exponents of the functions on its corners ($s = 0.108$ and $p = 0.016$) through an analysis of the bound state spectra of the composite system ($e^+ + C_2H_4$). In the SCF calculation we used the equilibrium geometry of the ground state ($R_{CC} = 1.339$ Å, $R_{CH} = 1.086$ Å, H-C-H = 117.6°).

Table I shows all the ionization potential energies of C_2H_4 in a frozen core approximation. Considering that the ground state of a free positronium is 6.803 eV, real positronium formation can happen in our model only for positron impact energies above 3.46 eV. This is in

TABLE I. Frozen orbital ionization potential (IP) energies.

Hole orbital	$1a_g$	$1b_{1u}$	$2a_g$	$2b_{1u}$	$1b_{2u}$	$3a_g$	$1b_{3g}$	$1b_{3u}$
IP (eV)	306.00	305.97	28.33	21.58	17.66	15.97	13.77	10.26

good agreement with the experimental value 3.7 eV. That means, for energies below 3.46 eV, the real positronium formation is forbidden, for energies between 3.46 and 6.97 eV only electrons taken from the $1b_{3u}$ orbital can give rise to real positronium formation, from 6.97 to 9.17 eV only electrons from the $1b_{3g}$ and $1b_{3u}$ orbitals contribute to this phenomenon, and so on. Since real positronium formation is not described in the SMC method, our results are expected to be reliable below 3.46 eV and whenever the real positronium formation channel is less important than the virtual one.

Figure 1 shows our calculated elastic integral cross sections in the static-plus-polarization approximation along with the experimental results of Ref. [10]. This figure also shows the cross sections obtained exclusively from the A_g symmetry. This symmetry is responsible for a Ramsauer-Townsend minimum at around 2 eV. At the static level of approximation for a molecule as C_2H_4, a repulsive potential is expected for all energies (inside the electronic charge, the positron experiences the potential of a net
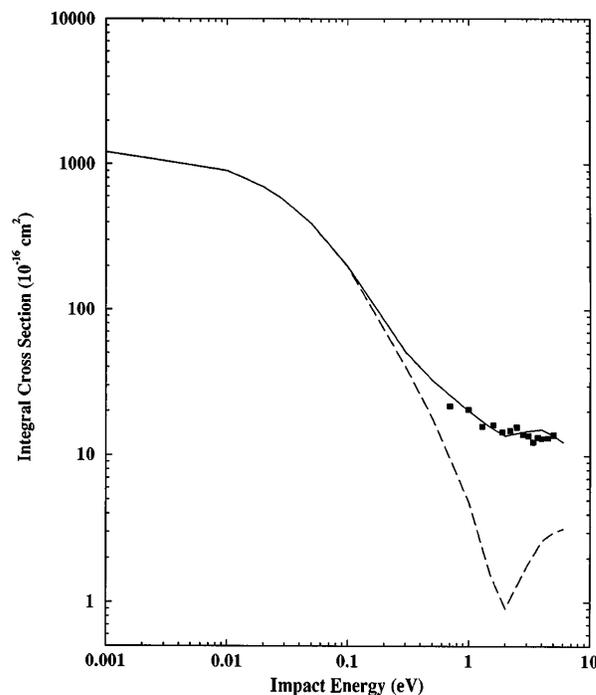

FIG. 1. Integral cross sections for e^+-C_2H_4 scattering. Solid line: our results including 23 112 configurations; dashed line: our results including 3294 configurations of the A_g symmetry; squares: experimental data of Ref. [10].

positive charge). At the asymptotic region the long range potential of C_2H_4 is due almost exclusively to polarization effects, and therefore it is attractive. The polarization potential strongly depends on the impact energy. Therefore when these effects are taken into account the overall potential may become on average attractive for low-energy scattering and repulsive as energy is increased. Although not shown in this Letter, we have confirmed this situation by analyzing the sign of the scattering eigenphases. In fact, here, the Ramsauer-Townsend minimum is attributed to a change in sign of the eigenphase (partial wave transition $\{\ell = 0, m = 0\} \rightarrow \{\ell' = 0, m' = 0\}$) and can be seen as a change of the overall potential from attractive to repulsive at around 2 eV. Usually, the Ramsauer-Townsend minimum is attributed to a potential that became so strong it pulls the eigenphase towards $\delta = \pi$ causing a zero contribution to the cross section (which depends on $\sin^2\delta$). In the present case, the phase shift caused by the attractive potential region is counterbalanced by the shift caused by the repulsive potential region (the positron sees on average a potential equal to zero).

Our overall integral cross sections agree very well with the experimental data of Ref. [10]. We only obtain such a good agreement when we include all symmetries (23 112 configurations) in our calculation. The other symmetries contribute strongly to the cross sections in this energy region, smoothing out the minimum structure shown in the A_g symmetry (3294 configurations). The excellent agreement of our cross sections with the experimental data is a good indication that our $(N + 1)$-particle wave function is reasonably well described and can be used in the calculation of the annihilation parameter Z_{eff}.

Figure 2 presents our annihilation parameter Z_{eff} as a function of the impact energy of the incoming positron. The only available experimental result [2] was obtained at room temperature (0.0257 eV). To compare our results with this experimental value we have averaged the $Z_{eff}(\vec{k}_i)$ of Eq. (3) over all directions of $\vec{k}_i$. The solid line in Fig. 2 represents our calculation including all symmetries. The dashed line is a calculation with only 3294 configurations of symmetry A_g. The A_g symmetry dominates completely the low-energy region as one could expect. In order to annihilate, the positron needs to get close to the molecule, and to do so it needs to overcome all angular momentum barriers. The A_g symmetry is the only symmetry that allows the positron to get close to the electronic charge independently of how small is the impact energy. This is because, in a partial wave decomposition, the A_g symmetry has contributions from the $\ell = 0$ wave (which provides no angular momentum barrier). The domination of the A_g symmetry over all the others at low energies is also seen in the cross sections, as shown in Fig. 1. Our results are in excellent agreement with the experimental point at room temperature and suggest that the annihilation parameter depends strongly on the temperature of the positron gas.
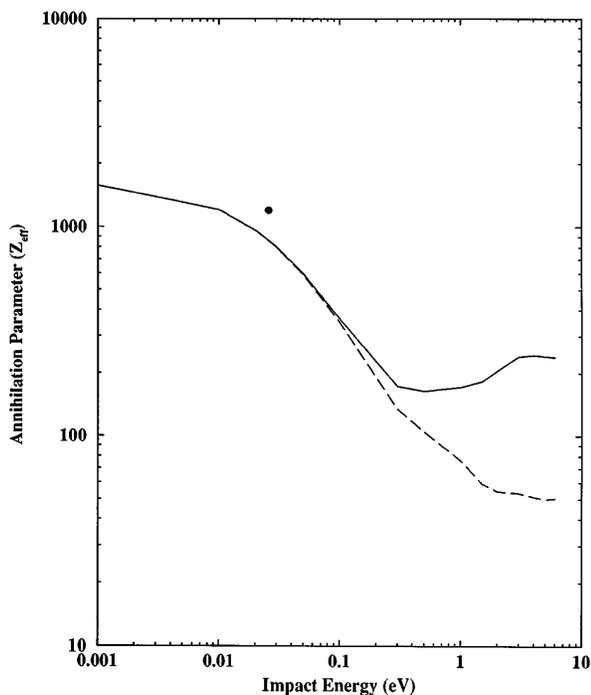

FIG. 2. Annihilation parameter Z_{eff} in e^+-C_2H_4 scattering. Solid line: our results including 23 112 configurations; dashed line: our results including 3294 configurations of the A_g symmetry; circle: experimental result of Ref. [2].
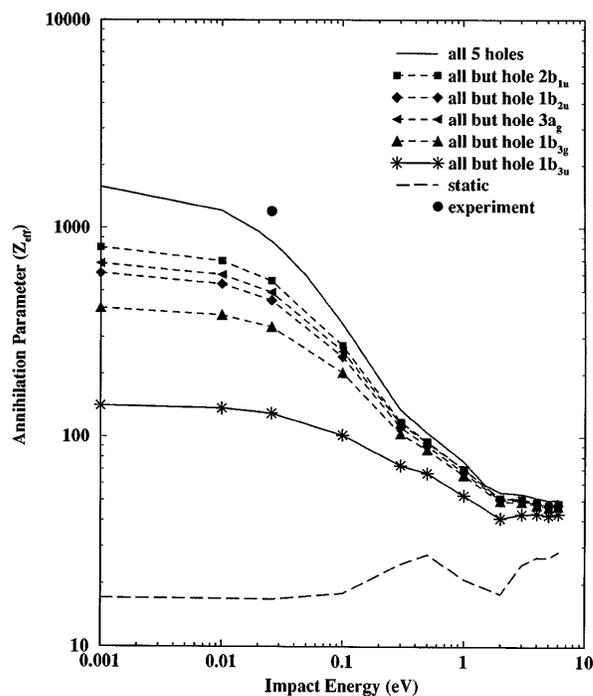

FIG. 3. Annihilation parameter Z_{eff} in e^+-C_2H_4 scattering at different levels of approximations (see text); circle: experimental result of Ref. [2].
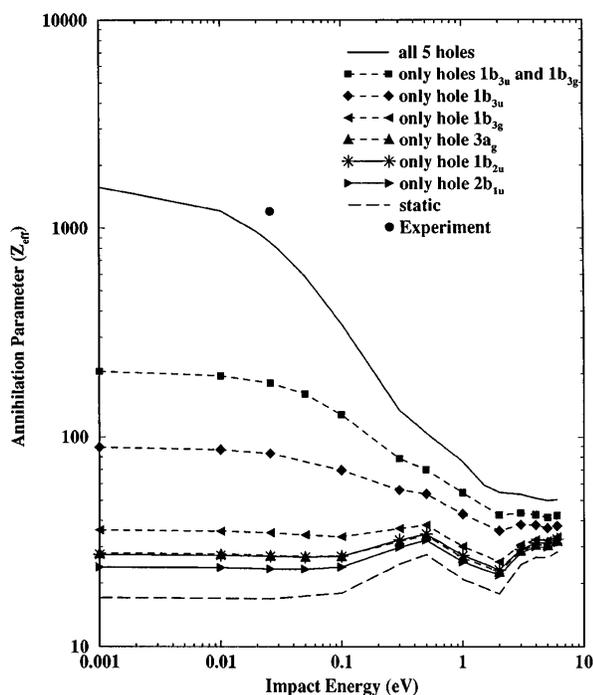
FIG. 4.   Same as in Fig. 3.

In Figs. 3 and 4, we present a study of the dependence of the Z_{eff} parameter with respect to different levels of approximations of the Q space. In these figures we present only the A_g symmetry contributions. The Z_{eff} in the static approximation ($Q = 0$) is very close to $Z = 16$ at all energies. The large increase of Z_{eff} at low energies is fully due to polarization effects. A simple perturbation theory would predict that excitations out of the shallowest orbitals are more important than those out of the deepest ones. That means we should expect that electrons of the $1b_{3u}$ orbital would have more important participation in possible virtual positronium formation than those of the other orbitals. In order to test this assumption we carried out a set of calculations leaving out of the Q space one by one of the 5 shallowest hole orbitals. As expected, and shown in Fig. 3, the most relevant absences are the excitations out of the $1b_{3u}$ hole. The order of importance of the hole orbitals is almost the same as predicted by perturbation theory (looking only at the ionization energies). The only exception is a slight inversion of importance seen between the $1b_{2u}$ and the

$3a_g$ hole orbitals. This first set of calculations indicated that the large increase in the Z_{eff} is probably due to a $1b_{3u}$ electron captured by the positron, forming a positronium in the molecular ion field. To confirm this assumption we carried out a second set of calculations considering only one hole orbital at a time. These results are shown in Fig. 4. Again a simple perturbation theory would almost predict the correct order of importance of each hole. The surprising result is that excitations out of the $1b_{3u}$ orbital, when forming the Q space by themselves, account only for 10% of the Z_{eff} at low energies. Excitations out of the other orbitals are very important and can be interpreted as a deformation of the molecular ion to better accommodate the virtual positronium in the ion field. The molecule acts as a trap of positrons.

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