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Positron collisions with targets of biological and technological relevance

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Positron collisions with targets of biological and technological relevance

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Abstract. In this work we present calculated cross sections for elastic scattering of low-energy positrons by molecules, obtained with the Schwinger multichannel method. We extended a previous study on the role of polarization effects in the positron-allene scattering and also present some preliminary results for positron collisions with cyclopentane. We also compare the differential cross sections of benzene and its azaderivative pyrimidine at selected energies, where similar angular behaviour was found.

1. Introduction

Positron physics attracts great interest due to its fundamental, technological and biological applications. Since many of its applications are based on basic interactions of positrons with molecules, positron-scattering studies have become a cornerstone towards understanding the underlying physics of these interactions [1, 2]. In recent years, thanks to the advent of better theoretical methodologies and computers to perform the simulations, theoretical positron-molecules studies have gained new breath. At the same time, experimental advances have considerably improved the available data [3].

However, positron scattering calculations can be a difficult task due to some intrinsic problems. For example, besides the inelastic process already observed in electron-scattering, the incoming positron can capture one of the electrons of the target to form positronium (Ps). Moreover, Ps formation can be responsible for a large amount of the total cross section for positron impact energies over the positronium formation threshold [4]. Even more troublesome, at energies below the Ps formation and electronic excitation thresholds, the agreement between the theoretical calculations and experimental data is far from good. This is mainly because the description of the polarization potential, which is crucial in the positron scattering due to the absence of exchange effects, is an extremely hard task for theoreticians.

In recent years, our group has put a lot of effort in order to provide some reliable results for positron scattering by molecules and systems of technological and biological relevance. For example, employing the Schwinger multichannel method [5, 6], we have performed extensive studies in order to improve the description of the polarization potential for two small non-polar molecules, allene [7] and silane [8]. In both works we have shown that the inclusion of extra functions in chargeless centers seems to improve the description of the polarization effects. This was corroborated by the analysis of the s-wave cross section and eigenphase. It is worth mentioning that for the first time a bound state was predicted by an *ab initio* positron-molecule scattering calculation [7]. We have also worked on the description of positron interactions with biological systems, such as the pyrimidine molecule [9] and tetrahydrofuran [10].

In this contribution we employed the Schwinger multichannel method to obtain calculated cross sections for positron scattering by molecules of technological and/or biological relevance. We will review and present additional results on the description of the polarization effects in the positron-allene scattering, and present some preliminary results for positron scattering by cyclopentane. The present cyclopentane cross sections will be compared with previous results for tetrahydrofuran (THF) due to the similarity of both molecules. Indeed, THF can be seen as a cyclopentane where one of the CH group is replaced by an O atom. Besides, we will also present a comparison between the differential cross sections (DCS) for positron scattering by benzene and pyrimidine.

The remainder of this paper is as follows. In the next section we will provide some of the theoretical details of the Schwinger multichanel method, then in section 3 the results will be presented and discussed. The last section will present a brief summary of our findings.

2. Methodology and theoretical details

The elastic cross sections presented here were calculated with the Schwinger multichannel method (SMC) as implemented for positron-molecule scattering. Since the method has been described in detail in several publications [5, 6], here we will only discuss those aspects of the SMC method that are relevant to the present calculations.

The working expression for the scattering amplitude is:

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

where $d_{mn} = \langle\chi_m|A^{(+)}|\chi_n\rangle$ and the $A^{(+)}$ operator is given by $A^{(+)} = Q\hat{H}Q + PVP - VG_P^{(+)}V$. $|S_{\vec{k}_{i,f}}\rangle$ is a solution of the unperturbed Hamiltonian H_0 (the target Hamiltonian plus the kinetic energy of the incoming positron) and is given by a product of a target state and a plane wave; V is the interaction potential between the incident positron and the electrons and nuclei of the target molecule; $|\chi_m\rangle$ is a set of $(N+1)$-particle configuration state functions used in the expansion of the trial scattering wave function, $\hat{H} = E - H$ is the collision energy minus the full Hamiltonian of the system ($H = H_0 + V$), P is a projection operator onto the open-channel space defined by the target eigenfunctions, and $G_P^{(+)}$ is the free-particle Green's function projected onto the P-space. Finally $Q = (\mathbb{1} - P)$ is the projector onto the closed electronic channels of the target.

In the static plus polarization approximation (SP), the direct space is composed by configuration state functions (CSFs) of the form:

$$|\chi_j\rangle = |\Phi_1\rangle \otimes |\varphi_j\rangle \oplus |\Phi_i\rangle \otimes |\varphi_j\rangle, \tag{2}$$

where $|\Phi_1\rangle$ represents the ground state of the molecule obtained at the Hartree-Fock (HF) level, $|\varphi_j\rangle$ is a single-particle orbital used to expand the positron scattering orbital (see below) and $|\Phi_i\rangle$ is obtained from virtual single excitations of the target from the hole (occupied) orbitals to a set of particle (unoccupied) orbitals. Thus, it is worth mentioning that the description of the polarization effects depends on the basis functions employed in the target description as well as on the configurations employed in the SP calculations. With the aim of making the reading clear, the specific details of each calculation will be provided in the next section along with the results.

3. Results

3.1. Small apolar molecules

Recently we have shown that the description of the polarization effects in positron scattering by allene [7] and silane [8] can be improved by the inclusion of extra functions in chargeless centers. In particular, for the allene molecule the inclusion of extra functions placed in the vertices of two hexagons lying in planes perpendicular to the molecular axis, and the inclusion of four extra centers along the CH bond, as shown in the left side of figure 1, improves the description of the polarization effects [7]. We have found that as the extra centers were included in the calculations the polarization effects seem to be better described, once the minimum present in the *s*-wave cross sections moved to higher energies. Moreover, the abrupt increase in the integral cross section (ICS) as the impact energy goes towards zero was initially characterized as a virtual state and then as a bound state, as the number of extras centers and of the configurations space functions were increased [7]. Here we present an extension of this work, where similar calculations have been carried out but with the extra functions placed in chargeless centers located at the vertices of two squares lying in planes perpendicular to the molecular axis, as shown in the right side of figure 1.

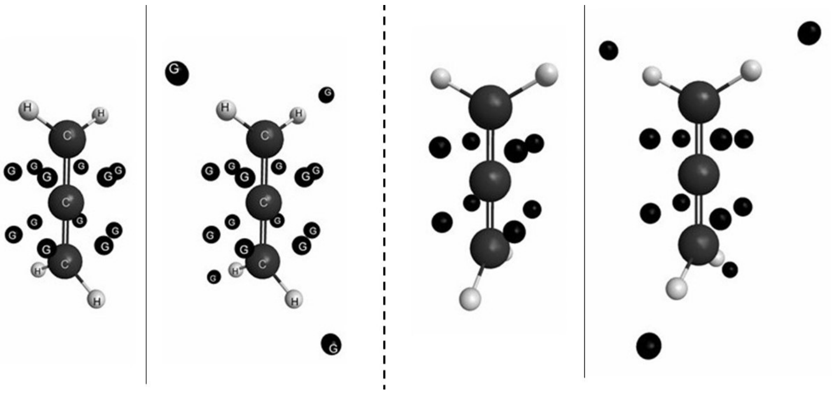

Figure 1. Geometrical structure of allene molecule and the position of the extra centers employed in the previous [7] (left) and present calculations.

The scattering calculations were carried employing the same geometry and basis set used in the previous study [7]. In all calculations, the 65 first modified virtual orbitals (MVO) [11] were employed as particle and scattering orbitals. The 11 valence orbitals were employed as hole orbitals and, with the 65 MVOs, as scattering orbitals. This is labelled as 65p76s along this text. The 0c-65p76s, hex-65p76s and hex+4-65p76s calculations correspond respectively to no extra centers, 12 extra centers placed in the vertices of two hexagons and 16 extra centers (the previous 12 and additional four extra centers placed along the CH bond). These calculations correspond to the SP-1, SP-3 and SP-5 presented previously [7]. Similarly, two other calculations labelled squa-65p76s and squa+4c-65p76s employed extra centers placed in the vertices of the two squares and with four additional centers along the CH bond, respectively. Since our aim is to discuss the low-energy physics of positron-allene scattering, we will present only the *s*-wave cross sections and eigenphases, which are presented in figure 2.

By inspection of figure 2 it is seen that the inclusion of the extra centers brings the minimum present in the cross section to higher energies, shifting it from 2.7 eV in the 0c-65p76s calculation to at around 3.3 eV. It is also noted that the cross sections obtained in the calculations employing extra centers, seem to overlap in the 0.5-5.0 eV energy region. Moreover, at the same energy the *s*-wave eigenphase changes sign from positive to negative. This is particularly related to the net potential felt by the incoming positron, which is a combination of the repulsive static potential and the attractive polarization potential. These two contributions cancel each other at the particular energy where the s-wave eigenphase changes sign (thus, the net potential changes from attractive to repulsive). Besides the minimum, the dramatic increase in the cross section as the impact energy goes to zero is also noticeable. This is a common feature in positron scattering and can be related either to a virtual or a bound state, depending on the behaviour of the s-wave eigenphase. Or, equivalently, the virtual or bound state is corroborated by the calculation of the scattering length (SL) defined as [12]

$$\mathrm{SL} = -\lim_{k \to 0} \frac{1}{k} \tan \delta_0(k) \tag{3}$$

where δ_0 and k are the s-wave eigenphase and the positron momentum, respectively. Thus, if the SL is positive (negative) a bound (virtual) state takes place.

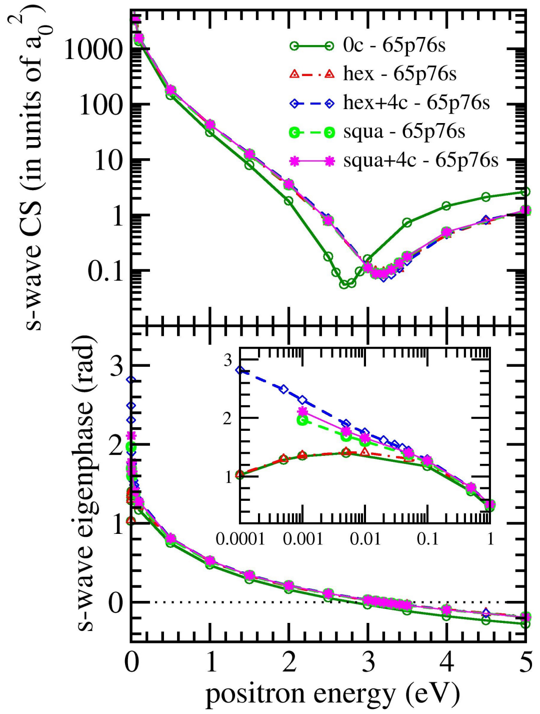

Figure 2. Positron scattering by allene: (top panel) s-wave cross section (CS) and (bottom panel) respective eigenphase calculated employing different schemes to account for the polarization effects. The inset presents the same data within a logarithmic energy scale, in order to highlight their very low-energy behavior. (hex = 2 hexagons = 12 extra centers; squa = 2 squares = 8 extra centers)

As discussed previously, the 0c- and hex- calculations support a virtual state, whereas the hex+4- calculation supports a bound state [7]. Moreover, we have also seen that only by increasing the configuration space by including more virtual single excitations of the target, the calculations employing 12 extra centers lead to a bound state [7]. Regarding the results obtained in the squa-65p76s and squa+4c-65p76s calculations, it is noted that at lower energies the s-wave eigenphase increases, presenting a similar behaviour to the hex+4c- case. The squa- and squa+4- calculations lead to SL equal to 256 a_0 and 183 a_0, respectively, supporting a bound state in both cases. That is, even employing a smaller basis set than previously, in the hex-65p76s calculation, the effective potential seems to be more attractive once a bound state is supported in squa-65p76s calculations. These results reveal the importance on the choice of the positions of the extra functions. This is noted by comparing the hex-65p76s and squa-65p76s results, which reveal that a reduced basis set (due to the lower number of extra functions employed in the latter calculation) can provide a better description of the polarization effects, in particular at impact energies lower than 0.1 eV. However, it should be noted that for higher impact energies, all calculations employing the extra functions seem to provide similar results regardless of the position of the extra functions.

3.2. Tetrahydrofuran and cyclopentane

Here we present preliminary calculated cross sections for low-energy positron scattering by cyclopentane (C_5H_{10}) and compare with the previous results for tetrahydrofuran (C_4H_8O). Both molecules are cyclic with five atoms in the ring and, as shown in figure 3, THF can be obtained by the replacement of a CH_2 group of cyclopentane by an oxygen atom. Besides this similarity it is important to note that whereas cyclopentane presents a dipole moment that is approximately zero, THF presents a dipole moment of 2.03 D [10]. Thus this difference shall play an important role in the positron scattering dynamics.

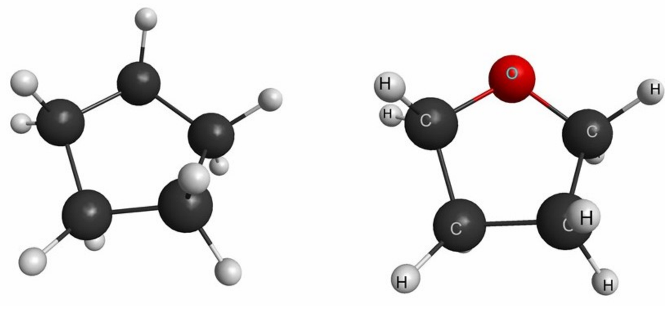

Figure 3. Geometrical structure cyclopentane (left) and tetrahydrofuran (right) molecules.

The scattering calculations for cyclopentane were carried out in the C_2 symmetry group following the same procedure as in our previous work on THF [10]. That is, the 15 outermost occupied orbitals were employed as hole orbitals, the 35 lowest MVOs [11] as particle orbitals and these MVOs along the 20 occupied orbitals were used as scattering orbitals. Besides this calculation, labelled SP-1, we also carried out two others where we have optimized the molecular geometry in the C_{2v} symmetry group. At this symmetry group all the carbon atoms lie in the same plane. Although not working in the ground state geometry, using a larger symmetry group permits the use of a larger number of CSFs in the calculation.

In figure 4 we present preliminary calculated integral cross sections for cyclopentane obtained in the C_2 and C_{2v} symmetry groups. In the C_{2v} symmetry group we carried out two calculations, the first one employing the same polarization scheme employed in the C_2 calculations (SP-1) and the second one (SP-2) employing the 15 valence orbitals as hole, the 55 lowest MVOs as particle orbitals and all the occupied orbitals with these 55 MVOs as scattering orbitals. The present results are compared with the available results for THF.

From figure 4 it is noted that both SP-1 calculations for the cyclopentane present an overall similar behaviour, where the main differences (e.g. the minimum at around 0.5 eV and the ICS magnitude at impact energies higher than 2.0 eV) are due to the different geometry employed in each calculation. This is better seen in figure 5 where the symmetry decomposition, according to the C_2 symmetry group, of the SP-1 calculated ICSs are presented. It should be noted that the only difference among these calculations is the employed molecular geometry. That is, the description of the polarization effects employed the same number of hole, particle and scattering

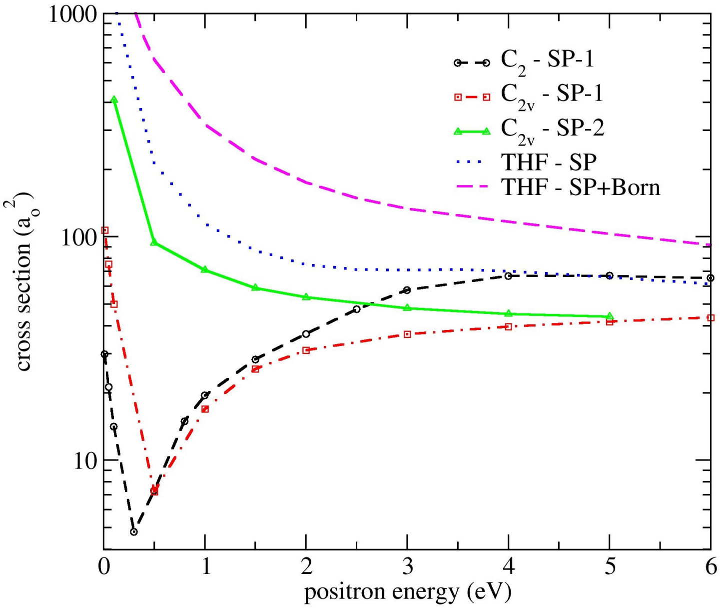

Figure 4. Calculated integral cross sections for elastic scattering of positrons by cyclopentane, in the static plus polarization approximation, obtained in the C_2 and C_{2v} symmetry groups. The present results are compared with the calculated results for THF in the SP and SP+Born approximations [10].

orbitals in each calculation. When comparing SP-1 and SP-2 calculations, carried out in the C_{2v} symmetry group, we observe that the ICS obtained in SP-2 scheme presents larger magnitudes. Moreover, the former results present a minimum at around 0.5 eV, whereas this minimum is not seen in the SP-2 results. From the comparison of the symmetry decomposition of the cross sections, in the C_{2v} symmetry group, presented in figure 6 it is seen that this is not only due to an improvement in the totally symmetric irreducible representation, A_1, but also in the B_1 and B_2 symmetries where a pronounced structure at around 1.0 eV is observed. As shown in the literature, this structure is due to an angular momentum barrier effect [13].

3.3. Pyrimidine and benzene

We have recently devoted some effort to the study of positron scattering by molecules of biological relevance including pyrimidine, one of the building blocks of the nitrogenated bases of DNA. Pyrimidine can be seen as a derivative of benzene with the replacement of two CH groups of benzene molecule by a N atom in the 1 and 3 positions. Thus, this section will be devoted to a comparison of the SMC results, in particular the differential cross sections, for pyrimidine and benzene. The scattering calculations were carried out in the optimized geometry of both molecules, as discussed previously [9, 14], in the C_{2v} symmetry group for pyrimidine and D_{2h} for benzene (although benzene belongs to the D_{6h} symmetry group, once the SMC method only deals with abelian groups). For the description of the polarization effects we have employed the 15 valence orbitals as hole orbitals, 50 MVOs as particle orbital and these 50 MVOs along the 21 occupied orbitals as scattering orbitals, resulting in a total of 53612 CSFs for pyrimidine and 53424 CSFs for benzene.

It have been shown in several references (see for example [15] and references therein) that the differential cross sections for electron scattering by benzene and the azaderivatives present similar oscillatory behaviour. Thus, it could be important to look for similarities and/or differences in

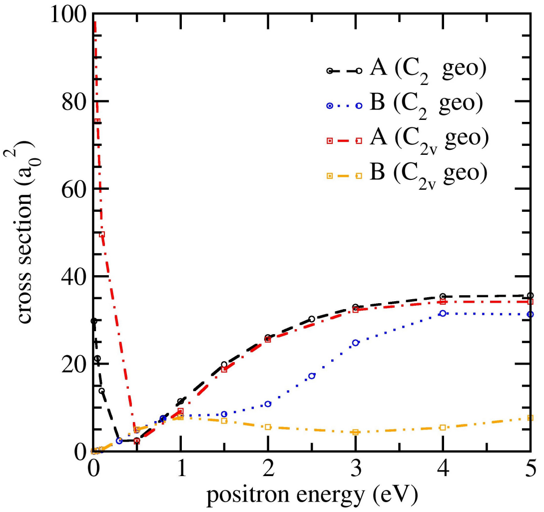

Figure 5. Symmetry decomposition, according to the C_2 symmetry group, of the SP-1 calculated integral cross sections for cyclopentane. It should be noted that the only difference among the calculations is the molecular geometry employed in the calculations.

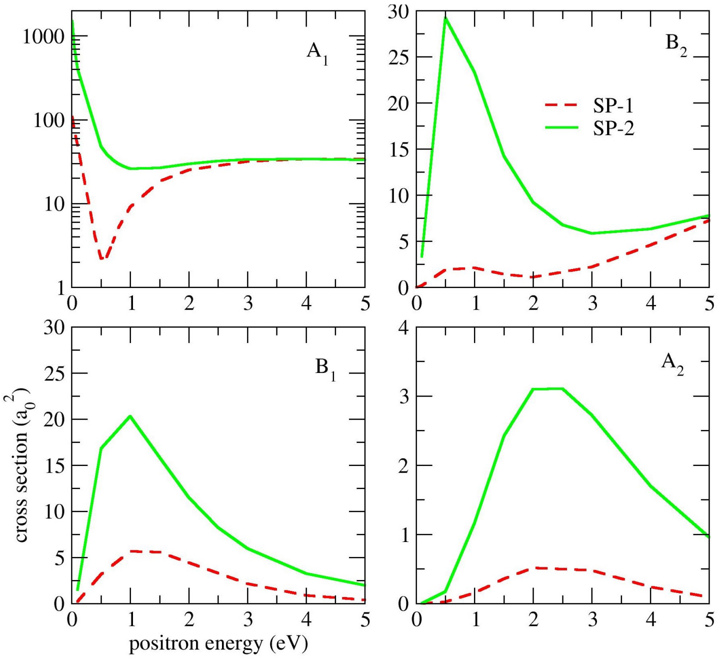

Figure 6. Symmetry decomposition, according to the C_{2v} symmetry group, of the calculated integral cross sections for elastic scattering of positrons by cyclopentane in the static plus polarization approximation, employing two different schemes (different numbers of CSFs).

the comparison of the DCS for positron scattering by benzene and its azaderivatives, such as pyrimidine. Figure 7 presents the differential cross sections for elastic scattering of positrons by benzene and pyrimidine at selected energies. The dashed black line corresponds to the SP calculations for benzene, whereas the solid cyan and the dot-dashed magenta lines correspond to the results for the pyrimidine molecule, obtained in the SP and SP+Born, where in the latter the long range effects of dipole moment potential are taken into account through the well known

Born-closure relation.

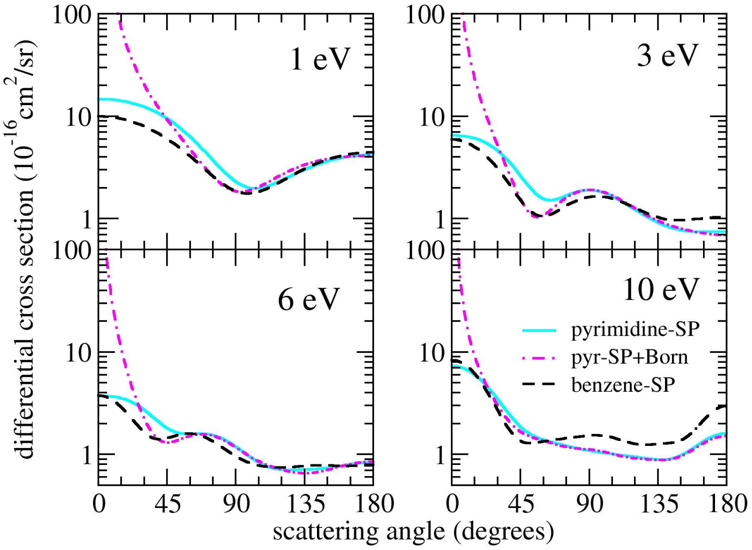

Figure 7. Calculated differential cross sections for elastic scattering of positrons by benzene and pyrimidine at selected energies.

From figure 7 it is seen that the main differences in the pyrimidine DCS in the SP and SP+Born approximations are in the low-angle region, which is a signature of the long range dipole moment potential. Moreover, when comparing benzene and pyrimidine cross sections, it is seen that the overall angular behaviour of the DCSs are very similar for both molecules at the SP approximations. On the other hand, they present differences at angles typically lower than 30 degrees when the Born correction for the long-range potential due to the dipole moment is included. It could be further interesting to study the DCS angular behaviour for positron scattering by other azaderivatives, such as pyridine where only one CH group in benzene ring is replaced by a N atom.

4. Summary

In this paper we have reviewed and extended some of our results in positron scattering by molecules obtained by employing the Schwinger multichannel method. We have discussed how the description of the polarization effects can be improved, either by including extra functions placed in chargeless centers or by enlarging the configuration space. In particular, we have seen that for the allene molecule, the position of the extra functions seems to play an important role in the description of the polarization effects, in particular at impact energies lower than 0.1 eV. This is based on the fact that the calculation employing functions in only eight extra centers (in the vertices of two squares) supports a bound state in positron-allene scattering, whereas the previous calculation employing functions in twelve extra centers (vertices of two hexagons) [7] supported a virtual state. For cyclopentane we have carried out calculations in the C_2 and C_{2v} symmetry groups (and, thus, employing molecular geometries optimized in these symmetry groups), where the latter calculations were carried out employing two different schemes for the SP approximation. It was noted that the C_2 and C_{2v} cross sections present an overall similar behavior when the same polarization scheme is employed, while the main differences, in particular the minimum at around 0.5 eV and the ICS magnitudes at impact energies higher than 2 eV, are due to the molecular geometry. Besides that, by enlarging of the CSFs space, in the SP-2 calculations, the ICS presents greater magnitude due to an angular momentum barrier effect. Finally, we have presented a comparison of the differential cross sections, at selected energies, for benzene and its azaderivative pyrimidine. We have seen that for both molecules the overall behaviour are quite similar, presenting more relevant differences in the low-angle region where the pyrimidine DCSs present an abrupt increase due to the long-range nature of the dipole moment potential. This study could be further extended by carrying out calculations for other azaderivatives, as pyridine.

Acknowledgments

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