

Elastic scattering of low-energy electrons by tetrahydropyran.

Alessandra Souza Barbosa^{1,2}, Márcio H. F. Betttega¹

¹ Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-990 Curitiba, Brazil

² Laboratório de Colisões Atômicas e Moleculares, CEFITEC, Departamento de Física, FCT Universidade Nova de Lisboa, 2829-516 Caparica, Portugal.

E-mail: asb07@fisica.ufpr.br; bettega@fisica.ufpr.br

Abstract. In this work we report calculated cross sections for elastic scattering of low-energy electrons by tetrahydropyran ($C_5H_{10}O$) molecule. We employed the Schwinger multichannel method (SMC) [5] implemented with pseudopotentials (SMCPP) in the static-exchange (SE) approximation for energies up to 30 eV. We compare our calculated cross sections with previous results obtained for cyclohexane and 1,4-dioxane molecules, since their geometrical structures are similar. We found that the differential cross sections obtained in the SE approximation present similar behavior for the three molecules except at lower angles, where the dipole moment present in tetrahydropyran increases abruptly the differential cross sections.

1. Introduction

Low-energy-electron collisions play an important role in many areas of interest, such as in high temperature plasmas and in biological systems. Regarding applications in high temperature plasmas one can highlight the fact that the cross sections resulting from the collisions of slow electron with molecules are used as input in modeling those plasmas [1, 2]. In biological systems the main effort is in the comprehension of electron interactions with molecules of biological interest, since low-energy electrons can cause single- and double-strand breaks to DNA [3].

The comparison of cross sections for electron collisions with similar molecules can provide useful information. Recently we showed that the calculated cross sections for elastic electron collisions with cyclohexane and 1,4-dioxane present some similarities among them [4]. These similarities were attributed to the geometrical structures of the molecules. In order to continue this study, we now compare tetrahydropyran cross sections with those obtained for the other close-related molecules. Tetrahydropyran and 1,4-dioxane can be seen as cyclohexane derivatives, with one or two oxygen atoms replacing the CH_2 groups. Although the three molecules present similar geometrical structures in the ground state, one should note that while 1,4-dioxane and cyclohexane do not have a permanent dipole moment, tetrahydropyran has.

In this work we report calculated cross sections for elastic scattering of low-energy electrons by the tetrahydropyran ($C_5H_{10}O$) molecule. We employed the Schwinger multichannel method (SMC) [5] implemented with norm-conserving pseudopotentials (SMCPP) [6] in the static-exchange (SE) approximation, for energies up to 30 eV. We compare our calculated cross sections with previous theoretical results obtained for cyclohexane [4] and 1,4-dioxane [7] molecules, since their geometrical structures are similar. In figure 1 we present the geometrical structures of



these three molecular targets. We also compare our calculated differential cross sections (DCSs) with experimental data available in the literature for electron collisions with 1,4-dioxane [8]. Regarding electron collisions with tetrahydropyran we only found one work reporting total cross sections (TCSs) [9] that could be compared with the theoretical elastic integral cross sections (ICSs) at lower energies. But, since this work only deals with the static-exchange approximation we choose not to do this comparison.

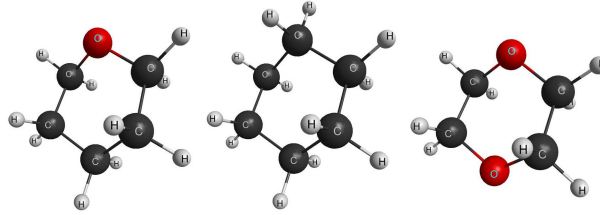


Figure 1. Geometrical structures of tetrahydropyran, cyclohexane and 1,4-dioxane molecules.

The remainder of this paper is as follows. In section 2 we present the theoretical method and computational procedure of this calculation. In section 3 we present and discuss the results. And in section 4 we close the paper with a brief summary of the present results.

2. Theory and computational details

Our calculations were carried out with the Schwinger multichannel method (SMC) [5, 10] with pseudopotentials [6]. The details of the method are not the main purpose of this work, here we will provide only the relevant points for the present calculations.

The SMC method is a variational approximation to the scattering amplitude. The resulting expression in the body-frame is given by:

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

where the set $\{|\chi_m\rangle\}$ represents a basis set of $(N + 1)$ -electron symmetry-adapted Slater determinants, also referred to as configuration state functions (CSFs). The CSFs are built from products of target states with single-particle wave functions. For the calculations carried out in the static-exchange (SE) approximation, the $(N + 1)$ -electron basis set (direct space) is given by

$$|\chi_m\rangle = \mathcal{A}(|\Phi_1\rangle \otimes |\varphi_m\rangle) \quad (2)$$

where $|\Phi_1\rangle$ is the target ground state, $|\varphi_m\rangle$ is a single-particle function and \mathcal{A} is the antisymmetrizer.

In Eq. 1, the d_{mn} matrix elements are given by

$$d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle \quad (3)$$

and the $A^{(+)}$ operator is given by

$$A^{(+)} = \frac{1}{2}(PV + VP) - VG_P^{(+)}V + \frac{\hat{H}}{N+1} - \frac{1}{2}(\hat{H}P + P\hat{H}) \quad (4)$$

In the above equations $S_{\vec{k}_{i(f)}}$ is a product of a target state and a plane wave with momentum $\vec{k}_{i(f)}$, which is an eigenstate of the unperturbed Hamiltonian H_0 ; V is the interaction potential between the incident electron and the target; $\hat{H} \equiv E - H$ is the collision energy minus the full

Hamiltonian of the system, with $H = H_0 + V$; P is a projection operator onto the open-channel space and $G_P^{(+)}$ is the free-particle Green's function projected on the P -space.

Our scattering calculations were carried out in the C_s point group employing the optimized ground-state geometry of tetrahydropyran. The geometry optimization employed the package GAMESS [12] at the second order Møller-Plesset Perturbation Theory using the TZV++(2d,1p) basis set. In figure 1 we present the geometrical structures of the tetrahydropyran along with 1,4-dioxane and cyclohexane. We used the norm-conserving pseudopotentials of Bachelet, Hamman and Schlüter [11] to replace the core electrons of the carbon and oxygen atoms. The valence target electrons are represented by Cartesian Gaussian functions which were generated according to [13]. The Cartesian Gaussian functions employed in this calculation were tabulated elsewhere [7]. The symmetric combinations of the d -type orbital were excluded to avoid linear dependency in the basis set.

The calculated dipole moment of tetrahydropyran is 1.74 D, which agrees relatively well with the experimental value of 1.58 D [15]. Since the SMC method employs only square integrable functions, when dealing with molecules that possess a permanent electric dipole moment, the long-range character of the dipole potential is truncated by the range of the Cartesian Gaussian functions, and therefore the higher partial waves are not properly described. To solve this problem, we included the dipole potential through a closure procedure described by de Oliveira *et al.* [16]. With this procedure the lower partial waves of the scattering amplitude are considered from the SMC method (we will call l_{SMC} the highest partial wave considered from the SMC method) and the higher partial waves are considered from the first Born approximation for the dipole moment potential of the molecule [16]. The number of lower partial waves included in the calculation depends on the energy and is chosen in order to provide the DCSs obtained with and without the Born closure correction in agreement at high scattering angles. We employed $l_{SMC} = 1$ from 0.1 to 0.6 eV, $l_{SMC} = 2$ from 0.7 to 1.8 eV, $l_{SMC} = 3$ from 1.9 to 2.9 eV, $l_{SMC} = 4$ from 3.0 to 5.0 eV, $l_{SMC} = 5$ from 5.1 to 6.2 eV, $l_{SMC} = 6$ from 6.3 to 14.0 eV, $l_{SMC} = 7$ from 14.5 to 16.5 eV and $l_{SMC} = 8$ from 17.0 to 30.0 eV.

3. Results

In the figure 2 we present our calculated integral and momentum transfer cross section (MTCS) in the SE approximation with and without the Born closure. We compare our ICSs and MTCSs with previous calculated results obtained for electron collisions with 1,4-dioxane [7] and cyclohexane [4], which were also obtained in the SE approximation. It is noted that the ICSs for the three molecules present similar behavior and magnitude except at lower energies where there is a great discrepancy between tetrahydropyran ICS and the other molecules ICSs due to the dipole moment of the molecule (indicated in the figure by "SE+Born"). One should note that the MTCS is less affected by the dipole moment correction due to the weight factor $(1 - \cos \theta)$, where θ is the scattering angle. By the similar behavior of the ICS and the MTCS for the three molecules we conclude that the molecular geometry may play an important role in the electron scattering cross section behavior. We also note, in figure 2, that the calculated cross sections in the SE approximation for the three molecules present a resonant structure at around 12 eV. With the inclusion of polarization effects we expect that this structure moves down in energy, such as we reported for cyclohexane [4] and 1,4-dioxane [7].

In the figure 3 we present the symmetry decomposition of the ICS for the three molecules according to the C_s group. The cyclohexane and 1,4-dioxane cross sections calculations were carried out within the C_{2h} symmetry group, and in order to compare their cross sections with the results for tetrahydropyran, we used the following relations between the symmetries of the two groups: $A' = A_g + B_u$ and $A'' = A_u + B_g$. It is worth mentioning that the structure present in the ICSs is due to the overlap of two structures belonging to the A' and the A'' symmetries of the C_s point group. In the A'' symmetry the structure is present at around the same energy for

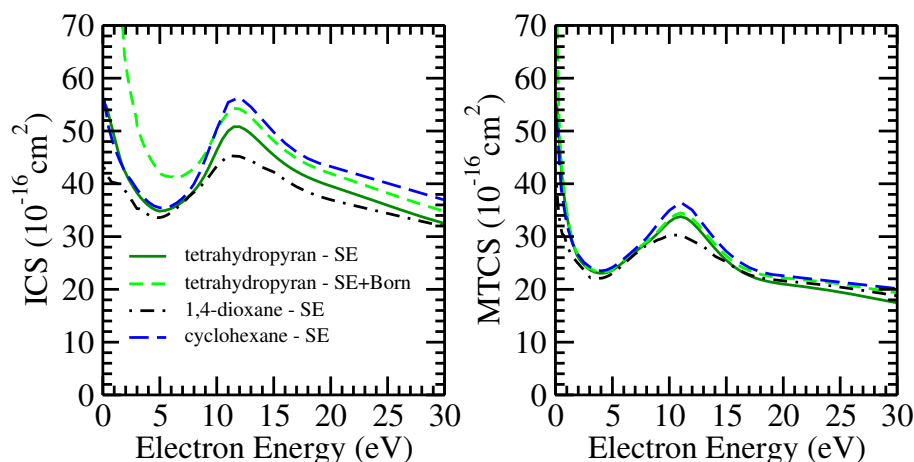


Figure 2. Integral Cross Section (left panel) and momentum transfer cross section (right panel) for elastic scattering of electrons by tetrahydropyran, in the SE approximation and in the SE approximation including the Born closure procedure. We also compare our results with calculated data for elastic scattering of electrons by 1,4-dioxane [7] and cyclohexane [4], only in the SE approximation.

the three molecules, while the A' symmetry ICS display a behavior somewhat different when one compares tetrahydropyran and cyclohexane cross sections with the 1,4-dioxane cross section.

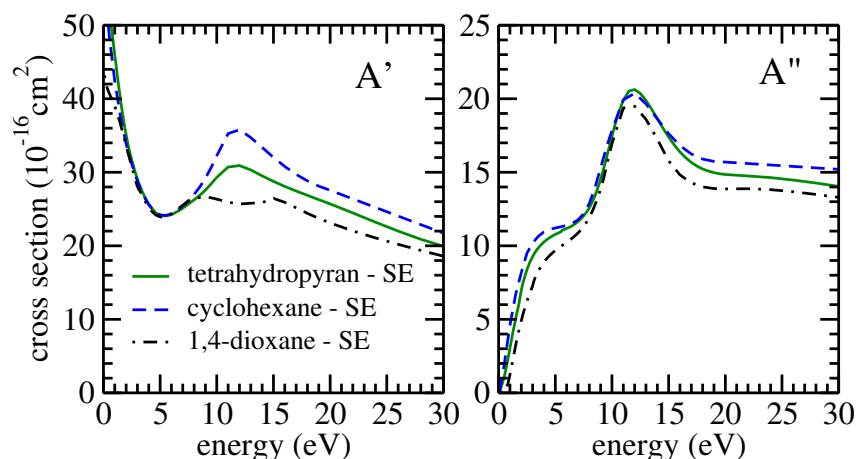


Figure 3. Symmetry decomposition according with C_s point group of the ICS for elastic scattering of electrons by tetrahydropyran. We compare the symmetry decomposition with previous data for 1,4-dioxane [7] and cyclohexane [4]. The calculated ICSs are presented in the SE approximation. See text for discussion.

In the figure 4 we present a comparison between the calculated differential cross sections for elastic scattering of electrons by tetrahydropyran, cyclohexane [4] and 1,4-dioxane [7] at 15, 20 and 30 eV. We also compare the calculated DCSs with experimental data available in the literature for elastic scattering of electrons by 1,4-dioxane [8]. One can note that the calculated DCSs are, in general, very similar in the oscillatory behavior and magnitude, presenting big discrepancies at lower angles where the dipole moment of the tetrahydropyran molecule increases the cross section abruptly. Regarding the comparison with the experimental data we found, in

general, a good agreement in the oscillatory behavior and the difference in magnitude is due to the pure elastic character of our calculations. It is known that the inclusion of inelastic channels permits flux loss, moving down the calculated elastic DCSs toward the experimental values.

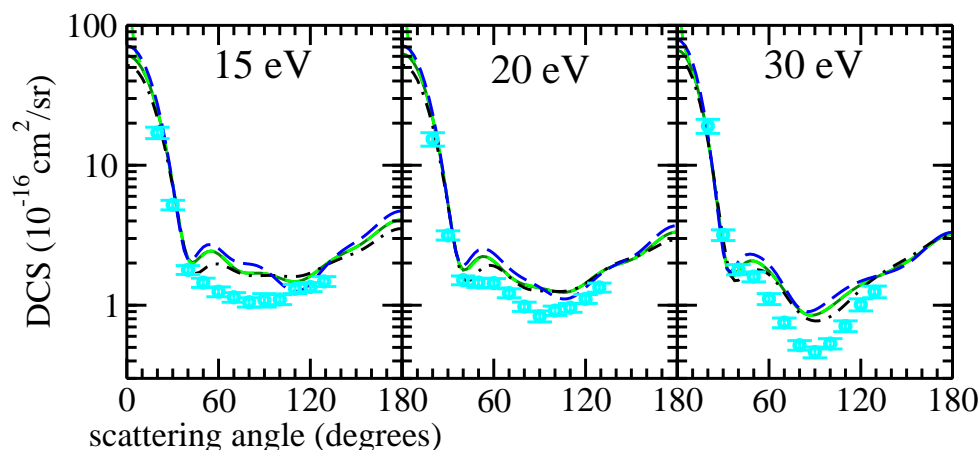


Figure 4. Differential cross sections for elastic scattering of electrons by tetrahydropyran at 15, 20 and 30 eV. Solid (dark green) line: present results; short dashed (green) line: present results including the Born closure procedure; long dashed (blue) line: cyclohexane [4]; dot-dashed (black) line: 1,4-dioxane [7]; circles (cyan): experimental results obtained for 1,4-dioxane [8]. All the calculated DCSs are presented in the SE approximation.

4. Conclusions

In this work we presented calculated cross sections, in the SE approximation, for electron collisions with tetrahydropyran and compared with previous data for 1,4-dioxane and cyclohexane due to the similarities in their geometrical structure. We showed that the geometrical structure of those molecules might play an important role in the electron scattering since their calculated cross sections present some similarities.

Acknowledgments

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