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Electronic excitation of the $^1B_2$ state of furan by electron impact

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Abstract. We report on recent results obtained in studies involving electronically inelastic electron scattering from furan. In particular, we considered the electronic transition from ground state to the $^1B_2$ excited state. The scattering calculations employed the Schwinger multichannel method implemented with pseudopotentials and were carried out up to a nine-state close-coupling plus polarization level of approximation.

1. Introduction

Experimental evidence showing that low-energy electrons can induce localized damage in the DNA strands [1, 2, 3, 4, 5] have triggered a growing interest in studies involving the interaction of electrons with molecules of biological relevance.

In this work, we consider the scattering of slow electrons by furan, one of the simplest heterocyclic coumpounds, which can be seen as an analog of 2-deoxyribose, the furanose sugar that links nucleic acids to phosphate groups in the DNA backbone. Electron interactions with furan have been subject of both experimental and theoretical investigations. In the measurements carried out by Flicker *et al.* [6], van Veen [7] and Giuliani and Hubin-Franskin [8] the electron energy loss spectroscopy (EELS) technique was used to study the electronically excited spectrum of furan. A series of EELS measurements were also performed by Motte-Tollet *et al.* [9] in order to investigate the resonant vibrational excitation of furan in its electronic ground state by low-energy electron impact. The results presented in their paper revealed the presence of a broad structure for the C-H stretching mode having its maximum centered at around 6 eV and assigned by the authors as a shape resonance with a σ^*(C-H) character. Through the use of the electron transmission spectroscopy (ETS) technique van Veen [7] and later, Modelli and Burrow [10], addressed the formation of temporary negative ion states in electron collisions with a variety of five-membered molecules. From these studies the occurrence of two π^* shape resonances located at 1.7 and 3.1 eV were observed in the scattering from furan molecules and attributed to the trapping of the incident electron in the lowest unoccupied molecular orbitals of the B_1 and A_2 symmetries of the C_{2v} point group, respectively. Work on dissociative electron attachment to heterocyclic coumpounds, including furan, were subject of very recent work performed by Muftakhov *et al.* [11, 12, 13, 14] and Sulzer *et al.* [16]. Dissociation and fragmentation processes leading to the formation of several electronically excited neutral atomic and molecular fragments in electron collisions with furan were investigated by Dampc and Zubek [15]. Finally, Szmytkowski *et al.* [17] measured absolute total cross sections (TCS) and also calculated elastic and ionization cross sections for electron scattering from furan molecules. Results obtained in their work indicated the presence of two sharp resonant peaks at 1.8 and 3.1 eV, a broad structure around 8 eV and less pronounced features at 5 and 14 eV.

Recently, we carried out a series of studies on elastic [18, 19] and electronically inelastic [20] electron collisions with furan. The work on elastic scattering were performed in a joint theoretical-experimental collaboration and, for this process, we obtained good agreement between measured and calculated cross sections, especially for energies below 10 eV. Resonant peaks located in our integral cross sections at the energies of 1.95 and 3.65 eV were in fully agreement with present [20], recent [17] and early [7, 10] experimental results. In Ref. [20] we investigate the influence of the inclusion of polarization effects in the description of the electronic excitation of furan by electron impact. The results obtained in that study showed that polarization effects can strongly influence electronic excitation cross sections for molecules supporting resonances near low-energy thresholds. As an extention of the work presented in our previous publications, in this paper we report on the $\tilde{X}^1A_1 \rightarrow {}^1B_2$ electronic transition in furan by electron impact. Integral and differential cross sections were calculated using the Schwinger multichannel method implemented with pseudopotentials. The scattering amplitudes were obtained up to a nine-state close-coupling plus polarization approximation in the energy range from 7.2 to 30 eV. The organization of the paper is as follows: in the next section some theoretical aspects of the Schwinger multichannel are briefly reviewed. In section 3, the computational details involved on target and scattering calculations are described. Results obtained in this work are presented and discussed in section 4 while, in section 5, we summarize our findings.

2. Theory

The scattering calculations presented in this paper were carried out using the Schwinger multichannel method (SMC) in its implementation with pseudopotentials (SMCPP). Detailed descriptions of the SMC and SMCPP methods have been given in previous publications (see, for instance, Refs. [21, 22, 23]) and, therefore, here we will present only a summary of the aspects which are relevant for the discussion following in the next sections. In the SMC method the total scattering wave function can be expanded in a trial basis set:

$$|\Psi^{(\pm)}_{\vec{k}}\rangle = a^{(\pm)}_m(\vec{k})|\chi_m\rangle \tag{1}$$

such as the variational determination of the coefficients $a^{(\pm)}_m(\vec{k})$ allows us to write:

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

which is the expression for the scattering amplitude in the body reference frame. In the above equation d_{mn} are matrix elements of the type:

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

where the $A^{(+)}$ operator can be written as:

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

In equations (2)-(4), $S_{\vec{k}_{i(f)}}$ is an eigenstate of the unperturbed Hamiltonian H_0, given by the product of a target state and a plane wave with momentum $\vec{k}_{i(f)}$; V is the interaction potential between the incident electron and the target; $\hat{H} \equiv E - H$ is the total energy of the collision 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. The χ_m's, also referred as configuration state functions (CSFs), are (N+1)-electron Slater determinants constructed from products of target electronic states and projectile scattering orbitals, and provide the basis for expansion of the trial scattering wave function given by Eq. (1).

The level of approximation of the scattering calculations is defined by the number of coupled channels entering the sum of energetically accessible states in P:

$$P = \sum_{l \in \text{open}} |\Phi_l\rangle\langle\Phi_l| \qquad (5)$$

and by the number of functions used in the composition of the configuration state space:

$$\{|\chi_m\rangle\} = \{|\chi_{ij}\rangle\} = \mathcal{A}_{N+1}\left[|\Phi_i(1,...,N)\rangle \otimes |\varphi_j(N+1)\rangle\right] \qquad (6)$$

where $|\Phi_i\rangle$ are N-electron Slater determinants obtained by single excitations from the occupied (hole) orbitals to a set of unoccupied (particle) orbitals. Finally, $|\varphi_j\rangle$ is represented by an one-electron wave function and $\mathcal{A}$ is the antisymmetrizer assuring the incoming electron to be indistinguisable from the target electrons.

3. Computational details

Furan is a typical representative of five-membered heterocyclic compounds consisting in a ring structure with four carbon atoms and one oxygen atom, as shown in Figure 1. The ground state of furan, $\tilde{X}^1A_1$, was computed in the Hartree-Fock approximation. Bound state and scattering calculations were performed within the C_{2v} point group at the experimental geometry of equilibrium [24]. The basis set employed in our study consists of square-integrable functions generated by a variational method described in Ref. [25]. For carbon atoms the basis set is composed by $5s5p2d$ uncontracted Cartesian Gaussian (CG) functions with exponents 12.49628, 2.470286, 0.614028, 0.184028, 0.039982, for the s–type functions; 5.228869, 1.592058, 0.568612, 0.210326, 0.072250, for the p–type functions and 0.603592, 0.156753 for the d–type functions. Oxygen atoms are described by a $5s5p2d$ set of uncontracted CG functions with exponents 16.05878, 5.920242, 1.034907, 0.316843, 0.065203 for the s–type functions; 10.14127, 2.783023, 0.841010, 0.232940, 0.052211 for the p–type functions and 0.756793, 0.180759 for the d–type functions. For hydrogen atoms we used the $4s$ (contracted to $3s$) basis set of Dunning [26]. Therefore, the one particle basis set employed in our calculations includes 176 primitive CG functions contracted to 172 functions.

The scattering amplitudes were generated in the scope of the minimal orbital basis for single configuration interactions (MOB-SCI) approach [30], as explained with more details in Ref. [20]. In summary, by applying the MOB-SCI strategy our active space for the SCI calculation was composed by the lowest $^3B_2$ and $^1B_2$ excited states along with a minimum set of pseudostates, which slightly polarizes the target. To properly account for the polarization of the target we have adopted the following procedure: by freezing the occupied orbitals and the active particle

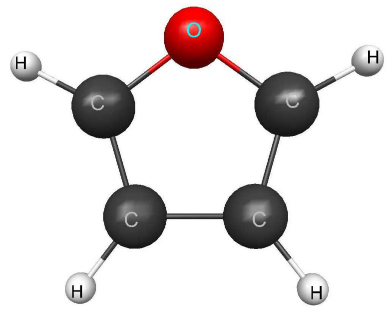

Figure 1. Geometrical structure of the furan molecule.

orbitals described above, we have diagonalized the cation Hamiltonian (more precisely a +2 cationic Fock operator where two electrons are subtracted from the a_2 occupied orbital) and generated modified virtual orbitals (MVOs) [27] from the remaining virtual orbitals. We then considered single excitations from all valence occupied orbitals to the MVOs with energies less than 15 Hartrees as a cut off criterion for selection of the particle orbital space. The same set of MVOs were then used as scattering orbitals. We included singlet and triplet excitations which resulted in a total of 18531 doublet CSFs distributed as follows: 4878 for the A_1 symmetry, 4391 for the B_1 symmetry, 4879 for the B_2 symmetry, and 4383 for A_2 symmetry.

4. Results

In Figure 2 we present the integral cross section (ICS) for the eletronic excitation of the $^1B_2$ state of furan by impact of slow electrons. The ICS curve displays a sharp raise at the threshold region and then increases more smoothly with the energy. The two peaked structures appearing at the energies of 8.9 and 9.8 eV are related with the thresholds of upcoming channels included in the active space of coupled states and, therefore, are considered as pseudoresonances. That is, the rapid variation observed in the ICS at these energies it is not related with the process of capture of the incident electron in a vacant molecular orbital, which is the physical picture related to the concept of a resonance. A slightly broader and less pronounced structure centered around 14 eV is also observed. This feature correlates very well with the shoulder visible on the TCS results measured by Szmytkowski *et al.* [17]. Based on the data for the negative-ion spectra for furan [11, 12, 13, 14, 16], these authors suggested that the shoulder may be assigned as a core-excited resonance. A deeper insight into the nature of this structure based on the analysis of our calculated cross section represents a subject for further investigation. Differential cross sections (DCS) covering the angular region from 0 to 180 degrees are shown in Figure 3. At the energy of 7.5 eV our DCS is nearly flat, displaying an almost s-wave like character. A more p-wave profile can be observed in the DCS at the energy of 8.0 eV. As expected, the importance of the contribution from higher partial waves is raised as the energy of the incident electron increases. For the energies of 9.0 and 10.0 eV the curves presents a larger number of undulations, characteristic of the presence of resonant structures (in this case, pseudoresonances), as indicated in the present integral cross section result.

The lack of experimental and/or theoretical data with which to compare our results prevents us to make a more detailed discussion on the cross section results for the electronic excitation of the $^1B_2$ state of furan by electron impact. Neverthless, it is important to mention that although not shown here, the ICS and DCS results for the transition involving the $^3B_2$ excited state obtained with the same computational model are in good agreement with the experimental data measured by Khakoo and co-workers [31], especially for energies up to 10 eV.

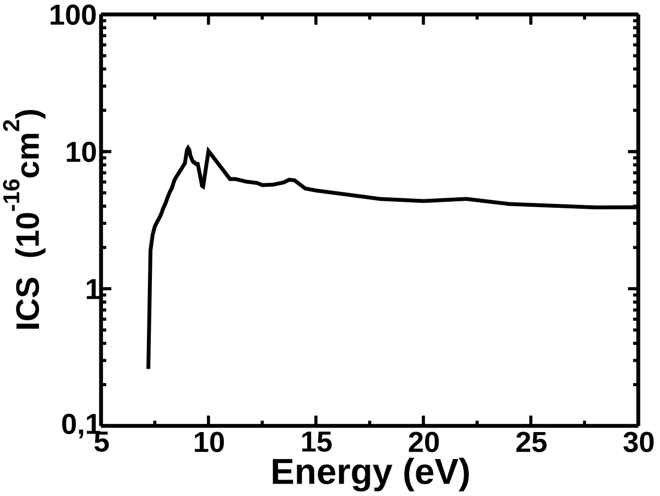

Figure 2. Integral cross section (ICS) for the electronic excitation from ground state to the $^1B_2$ state of furan by electron impact.

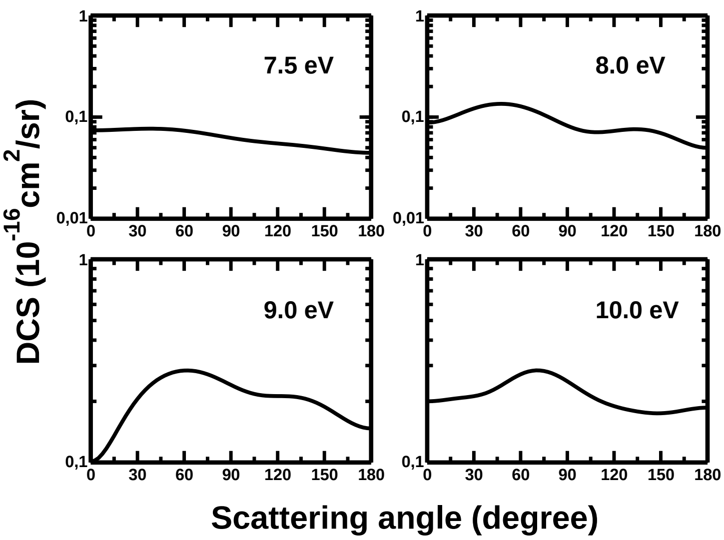

Figure 3. Differential cross sections (DCS) for the electronic excitation from ground state to the $^1B_2$ excited of furan by electron impact at the energies of 7.5, 8.0, 9.0 and 10.0 eV.

5. Concluding remarks

We have reported preliminary results on integral and differential cross sections for the $\tilde{X}^1A_1 \rightarrow {}^1B_2$ electronic transition in furan by electron impact. Integral and differential cross sections were calculated using the Schwinger multichannel method implemented with pseudopotentials. The scattering amplitudes were obtained up to a nine-state close-coupling plus polarization approximation in the energy range from 7.2 to 30 eV. The dependence of the calculated ICS shows three distinct peaked strucures in the energy region below to 15 eV. The two first pronounced features appearing at the energies of 8.9 and 9.8 eV are pseudoresonances related to the thresholds of coupled channels included in the sum of energetically acessible states to the target during the collion process. A weak structure is also observed and the position of its center is in good agreement with a shoulder appearing in the measurements reported in Ref. [17] and, tentatively assigned by these authors as a core-excited shape resonance. A more detailed investigation based on our scattering calculations and related to this specific issue based is under way.

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[31] *Private communication.* In fact, the study related with the electronic excitation of the $^3B_2$ and $^3A_1$ excited states of furan by electron impact has been developed in a collaborative project involving several groups from Brazil and one group in the USA.