

Electron collisions with the CH₂O-H₂O complex

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We report cross sections for elastic collisions of low-energy electrons with the CH₂O-H₂O complex. We employed the Schwinger multichannel method with pseudopotentials in the static-exchange and in the static-exchange-polarization approximations for energies from 0.1 to 20 eV. We considered four different hydrogen-bonded structures for the complex that were generated by classical Monte Carlo simulations. Our aim is to investigate the effect of the water molecule on the π^* shape resonance of formaldehyde. Previous studies reported a π^* shape resonance for CH₂O at around 1 eV. The resonance positions of the complexes appear at lower energies in all cases due to the mutual polarization between the two molecules. This indicates that the presence of water may favor dissociation by electron impact and may lead to an important effect on strand breaking in wet DNA by electron impact.

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The discovery by Boudaïffa *et al.* [1] that low-energy secondary electrons cause single and double strand breaking in DNA motivated several experimental and theoretical studies on electron collisions with biological molecules. This breaking is caused by the decay of a resonance and the subsequent bond (strand) breaking; this process is known as dissociative electron attachment (DEA). In particular, σ^* and π^* shape resonances play an important role in the DEA process [2,3]. However, most of the experiments and calculations consider these biological systems in the gas phase [4–6] and did not consider the influence of water. In order to investigate the influence of the water in the electron collisions with small systems that present a π^* shape resonance, we decided to look at the scattering of slow electrons by a small complex which is composed by one molecule of formaldehyde (CH₂O) and one molecule of water (H₂O). Our aim is to investigate what happens with the position of the π^* shape resonance when water is present and therefore contribute to the understanding of strand breaking in DNA. In the complex, these two molecules are bounded together by a hydrogen bond. CH₂O has a π^* (B_1) shape resonance at 1 eV as reported by the theoretical calculations of Rescigno *et al.* [7] and Kaur and Baluja [8]. H₂O is a well known target which has been investigated by several experimental and theoretical groups [9]. In particular, it has a broad shape resonance at around 10 eV. We considered four different structures of the complex which were obtained by classical Monte Carlo simulation of CH₂O in water environment at room temperature [10]. After the simulation statistically representative hydrogen-bonded complexes were sampled for electron collision targets. The present quantum-mechanical calculations performed on this complex take the mutual polarization between CH₂O and H₂O into account [10]. These structures are shown in Fig. 1 and do not correspond to minimum-energy structures.

In this paper we present momentum transfer cross sections for low-energy electron scattering CH₂O-H₂O complex.

Our calculations employed the Schwinger multichannel (SMC) method [11,12] with pseudopotentials [13] and were carried out in the static-exchange (SE) and in the static-exchange plus polarization (SEP) approximations. Our goal is to investigate the influence of the presence of one hydrogen-bonded water molecule in π^* shape resonance of CH₂O. We also carried out calculations for the CH₂O and H₂O molecules for purpose of comparison with the complexes results. The SMC method has been described in detail in several publications and here we will only discuss the relevant points to the present calculations.

In the SMC method the working expression for the scattering amplitude in the body frame (BF) is given by

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

where the $\{\chi_m\}$ represents a basis set of $(N+1)$ -electron Slater determinants [configuration state functions (CSFs)] which are constructed from products of target states with one-particle wave functions. $d_{mn} = \langle \chi_m | A^{(+)} | \chi_n \rangle$ and the $A^{(+)}$ operator can be written as

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

In the above equations $S_{\vec{k}_i(f)}$ 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.

For calculations carried out in the SE approximation, the

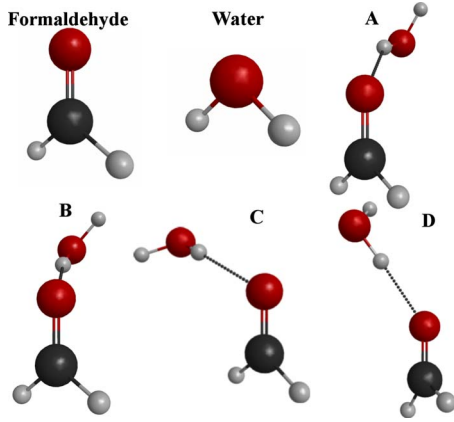


FIG. 1. (Color online) Geometrical structures of formaldehyde, water, and the four possible structures of the complexes (hydrogen-bonded pairs CH₂O-H₂O) named A, B, C, and D. These plots were generated using MACMOLPLT [15].

$(N+1)$ -electron basis set is constructed as $|\chi_m\rangle = \mathcal{A}|\Phi_1\rangle \otimes |\varphi_m\rangle$, where $|\Phi_1\rangle$ is the target ground state (represented by a single N -electron Slater determinant), $|\varphi_m\rangle$ is a one-electron function, and \mathcal{A} is the antisymmetrizer. For calculations carried out in the SEP approximation, the above set is enlarged by CSFs constructed as $|\chi_{mn}\rangle = \mathcal{A}|\Phi_m\rangle \otimes |\varphi_n\rangle$, where $|\Phi_m\rangle$ are N -electron Slater determinants obtained by single excitations from the occupied (hole) orbitals to a set of unoccupied (particle) orbitals. $|\varphi_n\rangle$ is also a one-electron function and \mathcal{A} is the antisymmetrizer. We kept only overall doublet states for the present closed-shell targets [14].

Our calculations considered four statistically representative structures of the CH₂O-H₂O hydrogen bond in the aqueous environment obtained by classical Monte Carlo simulations [10]. Figure 1 shows the geometric structure of CH₂O, H₂O, and the four structures for the CH₂O-H₂O complex we studied and named hereafter A, B, C, and D. We employed the *norm-conserving* pseudopotentials of Bachelet *et al.* [16] to replace the core electrons of carbon and oxygen. The Cartesian Gaussian functions used to represent the bound and the scattering orbitals for carbon and oxygen are from Ref. [17] and were generated according to Ref. [18]. The basis set for hydrogen was generated by Dunning [19] and was augmented with one p -type function with exponent 0.75. We have not included in our calculations the symmetric combinations of the d -type functions, namely, $[(x^2+y^2+z^2)\exp(-\alpha r^2)]$ in order to avoid linear dependency in the basis set. For the complexes all calculations were carried out in the C_1 group. For CH₂O and H₂O we performed calculations in the C_{2v} point group and also in the C_1 point group. We will discuss this point later.

We employed improved virtual orbitals (IVOs) [20] to represent the one-particle (particle and scattering) orbitals in the SEP calculations. For the complexes A to D we used all IVOs with energies less than 1 hartree as particle and scattering orbitals, and singlet- and triplet-coupled single excitations of the target. We obtained 5409 (doublets) CSFs for each structure. In order to describe the polarization effects for CH₂O and H₂O molecules in the same level as for the complex, we performed two different calculations: (i) CH₂O

and H₂O molecules without extra centers in the C_{2v} group; (ii) using the structure A for the complex for CH₂O considering the centers of H₂O as extra chargeless centers and using the structure A for the complex for H₂O considering the centers of CH₂O as extra chargeless centers. The second calculations were performed in the C_1 group. For the CH₂O molecule we used singlet and triplet coupled excitations for A_1 , B_2 , and A_2 . We used IVOs with energies less than 10 hartrees as particle and scattering orbitals and excitations out from the five highest occupied orbitals obtaining 6198 (doublets) CSFs for A_1 symmetry, 6015 (doublets) CSFs for the B_2 symmetry, and 5053 (doublets) CSFs for the A_2 . For B_1 we used only singlet coupled excitations and obtained 2669 (doublets) CSFs giving a total number of 19 935 CSFs. For the H₂O molecule we used singlet and triplet coupled excitations and obtained 2112 (doublets) CSFs for A_1 symmetry, 1737 (doublets) CSFs for B_1 symmetry, 1981 (doublets) CSFs for B_2 symmetry, 1612 (doublets) CSFs for A_2 symmetry, giving a total number of 7442 CSFs; all IVOs were used here as particle and scattering orbitals. For the CH₂O molecule with extra centers we used singlet and triplet coupled excitations and the same IVOs as in the complexes giving 4497 (doublets) CSFs. For the H₂O molecule with extra centers we used singlet and triplet coupled excitations and the same IVOs as in the complexes giving 3489 (doublets) CSFs. The dipole moments of water and formaldehyde are 2.006 D (1.9542 D with extra centers) and 2.926 D (2.928 D with extra centers), respectively, and of complexes A to D are 3.322 D, 4.440 D, 4.838 D, and 4.145 D, respectively. We also calculated the polarizabilities for H₂O, CH₂O, and for the complexes A to D with a DZV++ basis set with GAMESS and obtained (in units of a_0^3) 6.077, 14.034, 20.728, 21.117, 20.789, and 20.953, respectively. These values give an interaction polarizability ($\alpha_{inter} = \alpha_{complex} - \alpha_{formaldehyde} - \alpha_{water}$), which is the polarizability due to water on formaldehyde, of 0.617, 1.006, 0.678, and 0.842 a_0^3 , for complexes A to D. A more elaborated calculation by Fileti *et al.* [21] gives 27.01 a_0^3 for the CH₂O-H₂O complex, 17.58 a_0^3 for CH₂O, 9.30 a_0^3 for H₂O, and 0.13 a_0^3 for α_{inter} . To analyze the origin of some structures found in the cross sections, we followed a procedure proposed by Chaudhuri *et al.* [22].

In Fig. 2 we show the momentum transfer cross section for H₂O and CH₂O molecules with and without extra centers in the SE and SEP approximations. For H₂O there is a very broad structure at around 10 eV and a great increase in the cross section as the energy decreases. This structure appears around 10 eV in the experiment and theory of Khakoo *et al.* [9]. The present electron scattering by H₂O calculations have the only purpose of comparison, which will help in the understanding of the behavior of the cross section of the complexes. For CH₂O there is a π^* shape resonance at around 2.5 eV in the SE calculations which moves to around 1 eV with the inclusion of polarization effects. Our computed resonance position agrees well with previous calculations of Rescigno *et al.* [7] using the complex Kohn method and Kaur and Baluja [8] using the R -matrix method. However, some discrepancies were observed mainly in the behavior of the cross sections at lower energies. The results obtained by Rescigno *et al.* and by Kaur and Baluja display a rapid increase at lower energies. This behavior is not seen in our

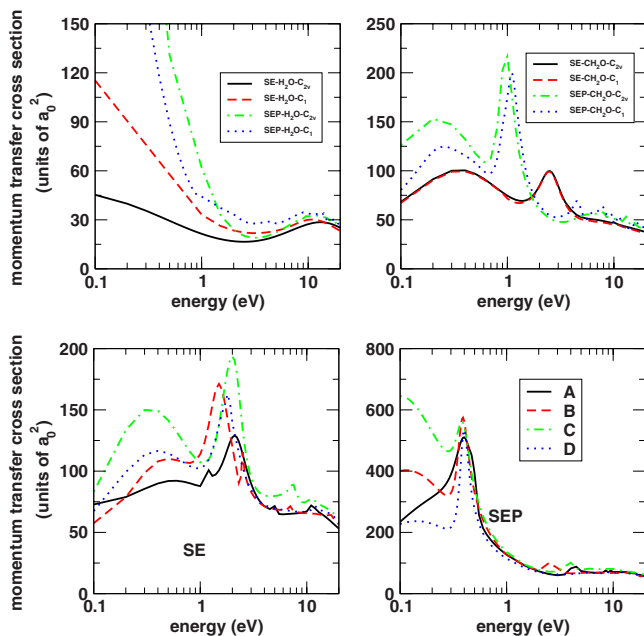


FIG. 2. (Color online) Momentum transfer cross sections for H₂O (left upper panel) and CH₂O (right upper panel) and for the four complexes (lower panels) in the SE and SEP approximations.

cross sections. We found out that the one-particle basis set employed in our calculations is not able to describe this behavior. We included some additional (chargeless) centers with diffuse functions and carried out calculations in the SE approximation. Our results display the low-energy increase in the cross section seen by the other two calculations. However, our results are smaller than the results of Rescigno *et al.* (SE) and Kaur and Baluja (eight-state CI calculation). Rescigno *et al.* computed only the B_1 symmetry using the Kohn method and included the remaining symmetries through the Born closure. This could explain the difference seen between our results and the results of Rescigno *et al.* With respect to the results of Kaur and Baluja, our present results also differ from theirs at lower energies, since our calculations do not describe the low-energy increase in the cross section, which has been already explained above. However, our results lie below the results of Kaur and Baluja and at this moment we have no explanation to this discrepancy, since Kaur and Baluja used another level of approximation to compute the cross sections and have not published any results in the SE approximation.

In the SE and SEP approximations the results for the calculations with and without extra centers for CH₂O agree well with each other placing the resonance at 2.5 eV and 1 eV, respectively. The differences seen in the SEP cross sections with and without extra centers are due to different number of CSFs employed in each calculation. For energies above 4 eV our SEP results display some pseudoresonances that can be attributed to closed channels that should be opened at those energies. Above ~ 5 eV the SE and SEP results become closer.

In Fig. 2 we also show the momentum transfer cross sections for the four complexes A, B, C, and D obtained in the SE and SEP approximations. All complexes present a reso-

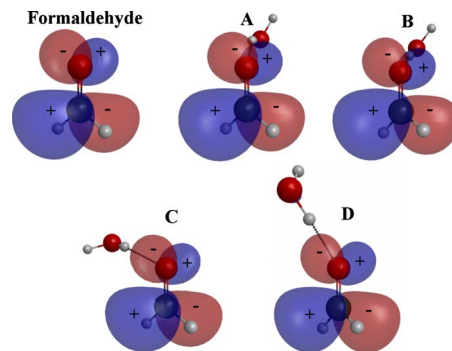


FIG. 3. (Color online) LUMOs for formaldehyde and the complexes A, B, C, and D. See text for discussion. These plots were generated using MACMOLPLT [15].

nance at around 2 eV in the SE calculations which moves to around 0.4 eV with the inclusion of polarization effects. The structure seen in each complex corresponds to the π^* shape resonance of the CH₂O and moves to lower energy in the complexes than in CH₂O due to the presence of water. The fact that the π^* shape resonance seen in the cross section of the complexes lies below the π^* shape resonance seen in the CH₂O cross section suggests that there is a polarization caused by the presence of water on formaldehyde (as discussed above).

In order to investigate the π^* character of the shape resonance of the complexes and to confirm that this resonance is the π^* resonance of CH₂O we looked at the lowest unoccupied molecular orbitals (LUMOs) plots of CH₂O and of each one of the four complexes. We carried out electronic structure calculations at the Hartree-Fock level using a (minimal) DZV basis set using GAMESS [23]. The results are shown in Fig. 3. According to these results the LUMO of CH₂O belongs to B_1 symmetry and is located at the C=O bond. For the four complexes the LUMOs have similar shape of CH₂O and are also located at the C=O bond.

Although not shown here, we also compared the sum of the integral cross sections of the CH₂O and H₂O molecules with the integral cross section of complexes A and C. The positions of the shape resonances of complexes A and C are lower than in the summed cross section suggesting that the complexes have a different behavior than the sum of its parts.

We presented momentum transfer cross sections for four different structures of hydrogen-bonded CH₂O-H₂O complex. We also calculated cross sections for CH₂O and H₂O molecules. CH₂O has a shape resonance at around 1 eV and H₂O shows a strong increase in the cross section as the energy decreases. The complexes present a resonance at around 0.4 eV, which corresponds to the π^* shape resonance of CH₂O. The resonance positions of the complexes appear at lower energies in all cases indicating that the presence of water may favor dissociation by electron impact. This phenomenon may lead to an important effect on strand breaking in wet DNA by electron impact. The present results, although carried out for a small molecule, represent a clear invitation for additional studies aiming resonant dissociation of wet biological molecules by low-energy electrons.

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