Potential energy surfaces for anion states of 5-chlorouracil

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Synopsis We present two-dimensional potential energy surfaces for the negative ions states π_1^*, π_2^* and σ_{CCl}^* of the potential radiosensetizer 5-chlorouracil. These were built along the C–Cl stretching mode (reactive coordinate) and an out-of-plane angular displacement of Cl atom (tuning coordinate), as obtained from scattering calculations performed with the Schwinger multichannel method. Analysis of the potential energy surfaces and quantum nuclear dynamics support that chloride elimination arises from an indirect mechanism around 1.5 eV, where the incoming electron is captured into a π^* orbital and is then transfered to the dissociative σ_{CCl}^* orbital.

Along the track of ionizing radiation large amounts of low-energy electrons are generated, which are very prone to be captured by biomolecules and trigger dissociative electron attachment (DEA) processes [1]. Halouracils, promising candidates for more efficient cancer therapies, are particularly susceptible to undergo DEA, which accounts for the radiosensitivity ability of these species [2]. However, the underlying molecular mechanisms for such process are still not well understood, and a more complete picture is required in order to fully explore the radiosensetizing activity.

When interacting with 5-chlorouracil, a low-energy electron may be imprisoned into delocalized π^* orbitals or into the localized σ_{CCl}^* orbital. At the neutral equilibrium geometry the character and energetics of the anion states were obtained by scattering calculations [3] and by electron transmission spectra measurements [4]. Here we present two-dimensional potential energy surfaces (PES) for the anion states of 5-chlorouracil, which allows for the evaluation of possible DEA mechanisms. The PES were built from a series of fixed-nuclei scattering calculations, performed with the Schwinger multichannel method implemented with pseudopotentials, in the static-exchange plus polarisation approximation.

Figure 1 shows the real component one-dimensional PES along the C–Cl stretching coordinate. Both π^* curves are nearly parallel to the neutral one, while the σ_{CCl}^* anion is clearly dissociative upon the bond stretching. The π^*/σ_{CCl}^* crossings suggest couplings between those states, which might explain the observed C–Cl bond breaking around 0 and 1.5 eV [2, 5, 6]. Since these couplings require a symmetry breaking vibration, an appropriate tuning coordinate must be taken into account, altogether with the reactive C–Cl coordinate. We considered the angular displacement of the chlorine atom away from the

molecular plane as the second dimension for the PES, which showed to efficiently mix π^* and σ_{CCl}^* orbitals. Nuclear quantum dynamics performed on the PES provides estimates for the DEA cross sections.
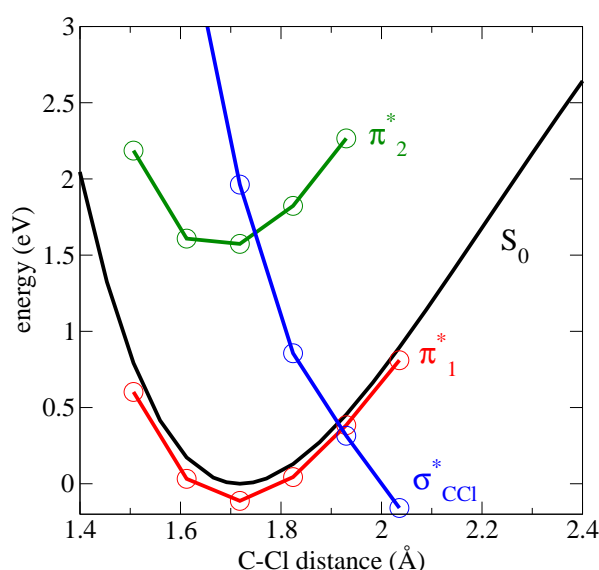

Figure 1. Potential energy curves for π^* and σ_{CCl}^* anion states and the neutral ground state of 5-chlorouracil, obtained along the C–Cl stretching coordinate.

References

[1] Boudaïffa *et al* 2000 *Science* **287** 1658

[2] H. Abdoul-Carime *et al* 2001 *J. Am. Chem. Soc.* **123** 5354

[3] F. Kossoski *et al* 2014 *J. Chem. Phys.* **140** 024317

[4] A. Scheer *et al* 2004 *Phys. Rev. Lett.* **92** 068102

[5] S. Denifl *et al* 2003 *J. Chem. Phys.* **118** 4107

[6] R. Abouaf and H. Dunet 2005 *Eur. Phys. J. D* **35** 405

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