

# New insights into electronic resonances of pyrrole derived from complex absorbing potential calculations

Madhubani Mukherjee and Anna I. Krylov

Department of Chemistry, University of Southern California, Los Angeles, USA

[mmukherj@usc.edu](mailto:mmukherj@usc.edu)

## Abstract

Dissociative electron attachment (DEA) is responsible for radiation damage to genetic material.<sup>1</sup> We chose pyrrole to study DEA because it is a small symmetric organic molecule structurally similar to the nucleobases. Several studies investigated the existence of a  $\sigma^*$  resonance in pyrrole which may lead to DEA and N-H bond breaking but the findings were contradictory.<sup>2</sup> We identified four resonance states in pyrrole, including the one that leads to the N-H bond breaking. We employed the equation-of-motion coupled-cluster method augmented by the complex absorbing potential (CAP) to describe electronically metastable states. The resonance wavefunctions were analyzed using Dyson orbitals. Along with the  $\pi^*$  resonances, we observed a low-lying electron attached state of mixed dipole supported and  $\sigma^*$  character. We constructed the potential energy surfaces along the N-H bond, optimized the equilibrium geometry of the resonance states and crossing between the lowest resonance of mixed character and the neutral. Our results are robust and  $\sigma^*$  resonances persist in different treatments (e.g., box CAP and Voronoi CAP). Three out of four resonance states were reaffirmed by the complex basis functions calculations. We posit that the electron can be attached to any of the resonance states and then cascades to the lowest resonance state with mixed character through non-adiabatic transitions causing the N-H bond dissociation. There are signatures of these resonance states in the experiments as well. To compare with experimentally observed features, we calculated the Franck-Condon factors between the resonance states and the neutral species, and theoretically simulated the electron energy loss spectra. Our simulated spectra agree to a large extent to the experimental spectra.

## References

- 1 E. M. de Oliveira, M. A. P. Lima, M. H. F. Bettega, S. d'A. Sanchez, R. F. da Costa and M. T. do N. Varella, *J. Chem. Phys.*, 2010, **132**, 204301.
- 2 A. Modelli and P. D. Burrow, *J. Phys. Chem. A*, 2004, **108**, 5721–5726.