Spectroscopic signatures of states in the continuum characterized by a joint experimental and theoretical study of pyrrole

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Dissociative electron attachment (DEA) occurs in high energy environment and it is responsible for radiation damage to genetic material.[1] We chose pyrrole to study DEA because it is a small organic molecule structurally similar to the nucleobases. Several studies investigated the existence of a σ* resonance in pyrrole which may lead to DEA and N-H bond breaking but the findings were contradictory.[2] 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 π* resonances, we observed a low-lying electron attached state of mixed dipole supported and σ* 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 show that σ* 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. There are signatures of these resonance states in the experiments as well. To compare with experimentally observed features, we simulated electron energy loss spectra (EELS) arising due to threshold excitation and due to resonances. The threshold excitation spectra were modelled with the Born approximation and the EELS due to resonance were simulated by computing Franck- Condon factors between the resonances and the neutral species. We proposed different models to compute the EELS arising from resonances. These spectra reveal several decay channels for the electron loss from the resonances. Our results agree well with the experimental ones.

References

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