

# Using nonadiabatic surface-hopping dynamics in order to understand the excited state electronic structure of pyrrole

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Pyrrole is a prototype example of a molecule displaying  $\pi\sigma^*$  mediated internal conversion. Recent experiments have shown that the time scale of this process is dependent on the wavelength of the initial excitation [1]. To better understand this effect, we have performed nonadiabatic surface-hopping dynamics simulations of the relaxation of pyrrole following excitation in three different energy regions [2].

The primary state populated in the  $\approx 200$  nm wavelength region is the lowest  $B_2$  state. Historically, this state has been described both as a pure Rydberg  $3p_x$  state and as a pure  $\pi\pi^*$  state. We have shown in our simulations that the results of the dynamics simulations are highly dependent on the description of this state in the chosen electronic structure method. Specifically, agreement with experiment is only achieved when no Rydberg-valence mixing is present in the description of the state. We also show preliminary simulations suggesting photoelectron spectroscopy as another experimental observable sensitive to the electronic structure of this state.

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## References

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