

Tailoring Attosecond Charge Migration in Native Molecular Ions

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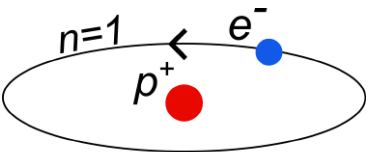
Supervisors: V. Despré (TheoChem) & F. Lépine (Dynamo)



Timescale of the Electronic Motion

Electrons motion is at the origin of nearly all our modern technologies (electronics, chemistry, etc.)

Bohr Model



~ 250 as

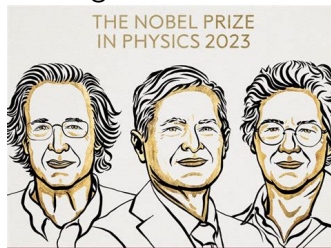
Few eV energy scale

\approx

1 fs – 10 fs timescale

1 as = 10^{-18} s

”For their work on attosecond pulses generation.”

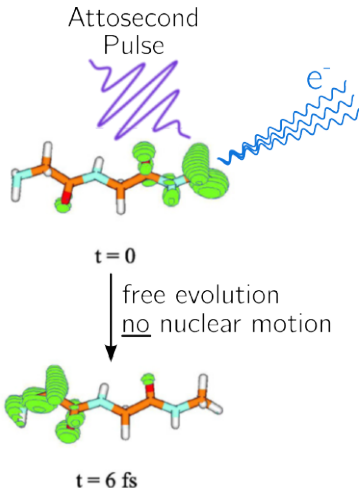
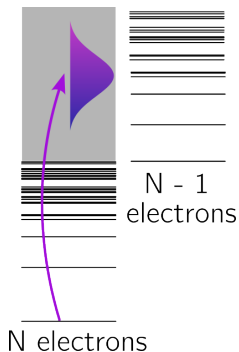


Allow to make physics in any system made of electrons (atoms, molecules, biomolecules, DNA, proteins,...)

Hole Migration in Molecules

Attosecond Pulse

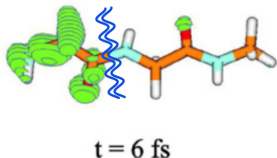
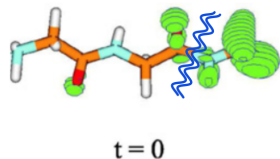
- 1 High photon energy
- 2 Large spectral width



Kuleff, A. I., Lünemann, S., Cederbaum, L. S.,
Chem. Phys (2013)

Correlation-Driven Dynamics

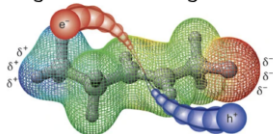
Charge Directed Reactivity



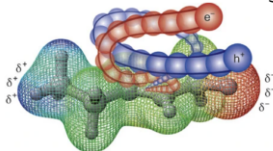
Remacle, F., Levine, R. D., Ratner, M. A.,
Chem. Phys. Lett. (1998)

Probe Electron Entanglement

Neglected Entanglement



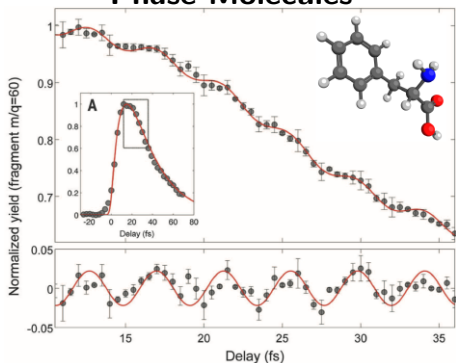
Real Motion of the Charge



Dutoi, A. D., Wormit, M. Cederbaum, L. S.,
J. Chem. Phys. (2011)

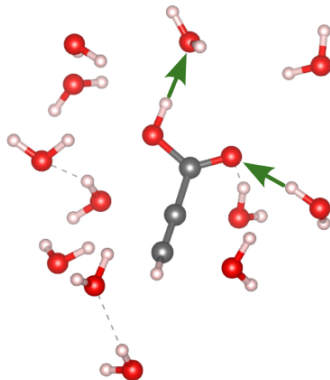
Where are we today?

Electron Dynamic in Gas Phase Molecules



Calegari, F., *et al*, *Science* (2014)

What about molecules with an environment?



In general molecules are charged when embedded in an environment

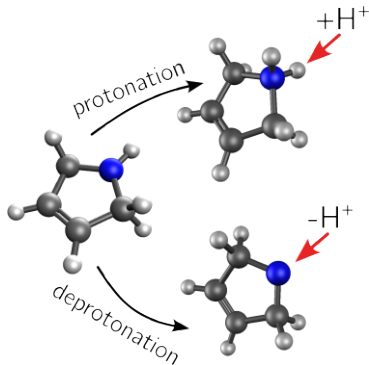
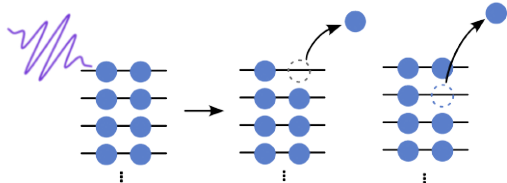
Charge Migration in Native Ions

Does hole migration survive if the molecule carries a native charge?

If yes, can the charge be used to control the hole migration?

Constraints of the Study:

- 1 Charge introduced by protonation and deprotonation
- 2 Focus on outer-valence ionization
- 3 Migration coming from entanglement



Electronic Structure

nD-ADC(3)/cc-pVDZ

Ionized States Perturbation Theory

$$\mathbf{G}(\omega) = \text{[Diagram 1]} + \text{[Diagram 2]} + \text{[Diagram 3]} + \dots$$

↓ nD-ADC(3)

$$\hat{H}_{\text{elec}}$$

Schirmer, J., Trofimov, A. B., Stelter, G., *J. Chem. Phys.* (1998)

Dynamics

Lanczos propagation

$$U(\Delta t) = e^{-i\hat{H}_{\text{elec}}\Delta t}$$

Allow to compute observables at each time-step

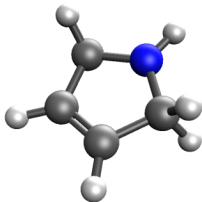
Electron Density:

$$n(\mathbf{r}, t) = \langle \Psi(t) | \hat{n}(\mathbf{r}) | \Psi(t) \rangle$$

Kuleff, A. I., Breidbach, J., Cederbaum, L. S., *J. Chem. Phys.* (2005)

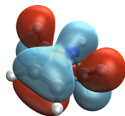
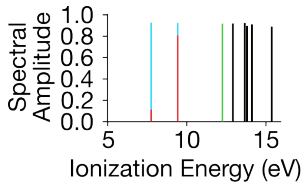
Reference: Neutral 3-Pyrroline

3-pyrroline
(neutral)

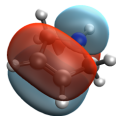


Can be both
protonated and
deprotonated on the
same site

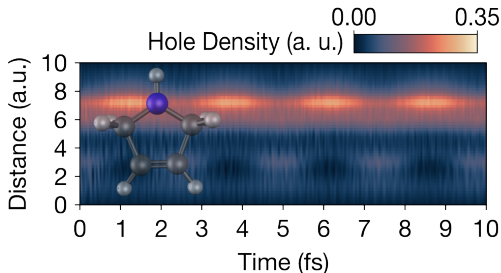
Scheidegger, A., Vaníček, J.,
and Golubev, N. V.,
J. Chem. Phys. (2022)



HOMO

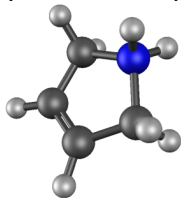


HOMO-1



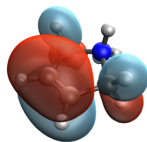
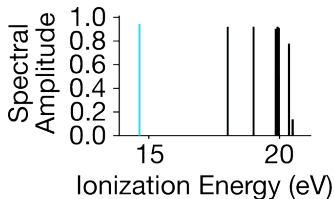
Protonation Suppress the Dynamics

3-pyrroline (protonated)

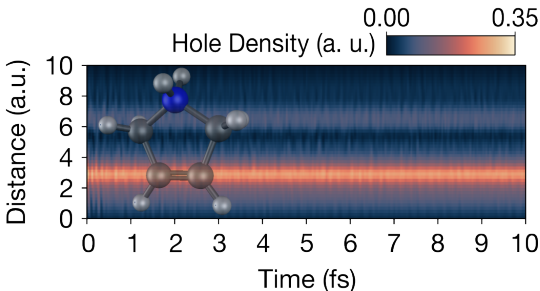


No more hole
mixing!

Always the case for
all the molecules
tested

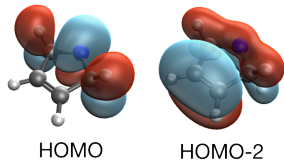
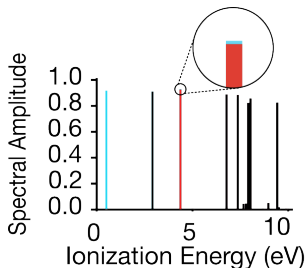
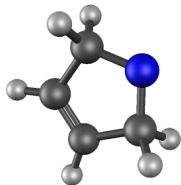


HOMO

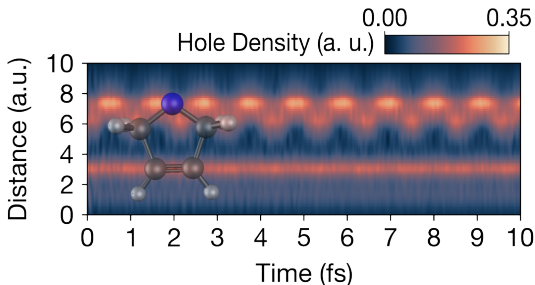


Deprotonation Accelerate the Dynamics

3-pyrroline (deprotonated)



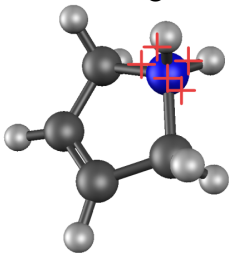
Accelerated hole
migration!



Impact of the charge localization

Protonation

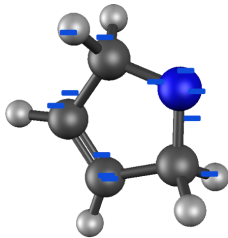
Additional Charge: Proton



Strong Local Impact

Deprotonation

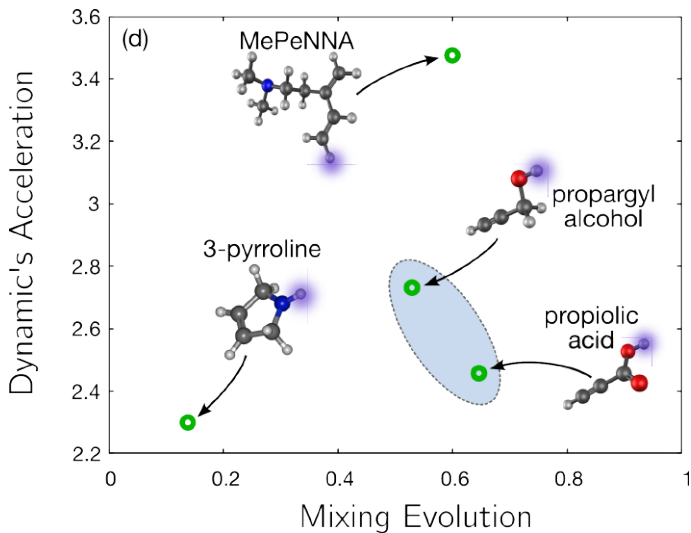
Additional Charge: Electron



The electron can delocalize over the molecule

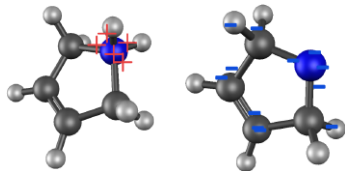
Should be molecule-dependent for deprotonation

What about other molecules?



Answers to our Questions

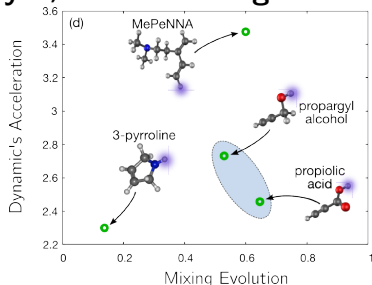
Does hole migration survive (outer-valence ionization) if the molecule carries a native charge?



Protonated Molecule: **No**

Deprotonated Molecules: **Yes**

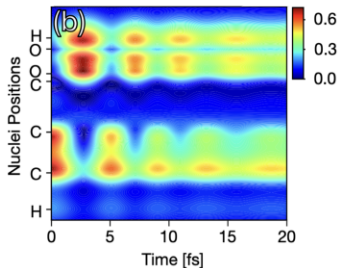
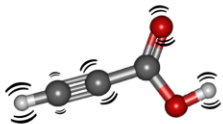
If yes, can the charge be used to control the hole migration?



Maybe, in deprotonated molecules

Outlooks

Take nuclear motion into account



Explicitly take the environment into account

