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Influence of an Oriented External Electric Field on Double Proton Transfer Reactions

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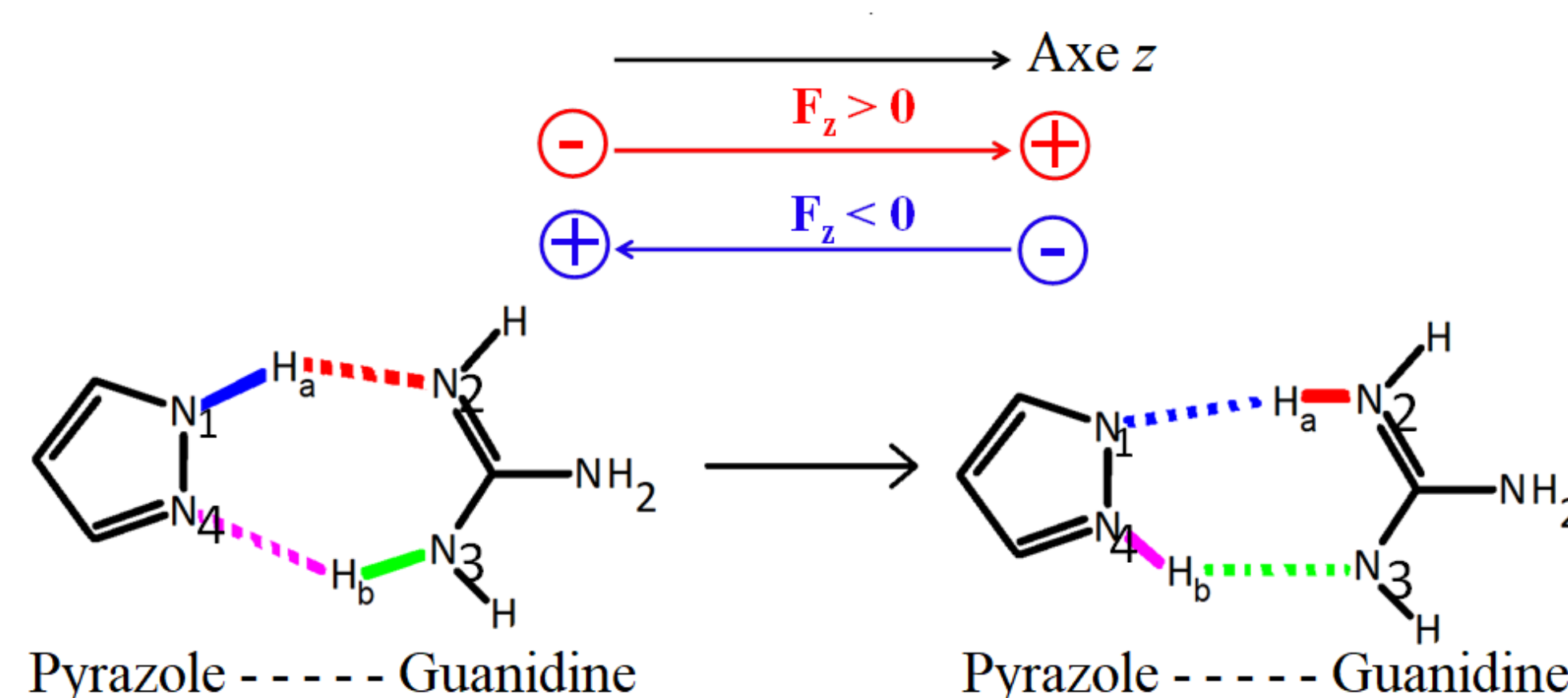
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1. Introduction

Work dealing with the influence of an oriented external electric field (OEEF) on the reactivity of organic compounds has increased in recent years. This type of external stimulus, called a "smart reagent", makes it possible to control the kinetics and selectivity of a reaction.[1] In this study,[2] we investigated the influence of an OEEF on the mechanism of double proton transfer in the pyrazole-guanidine complex. This reaction is concerted in the absence of an OEEF, but its potential energy profile exhibits a broad plateau in the region of the transition state, suggesting a strongly asynchronous mechanism.[3]

2. Conventions and methods

The reaction studied is the double proton transfer in the pyrazole-guanidine complex under electric fields F_z from 0 to 100×10^{-4} au along the proton transfer axis.

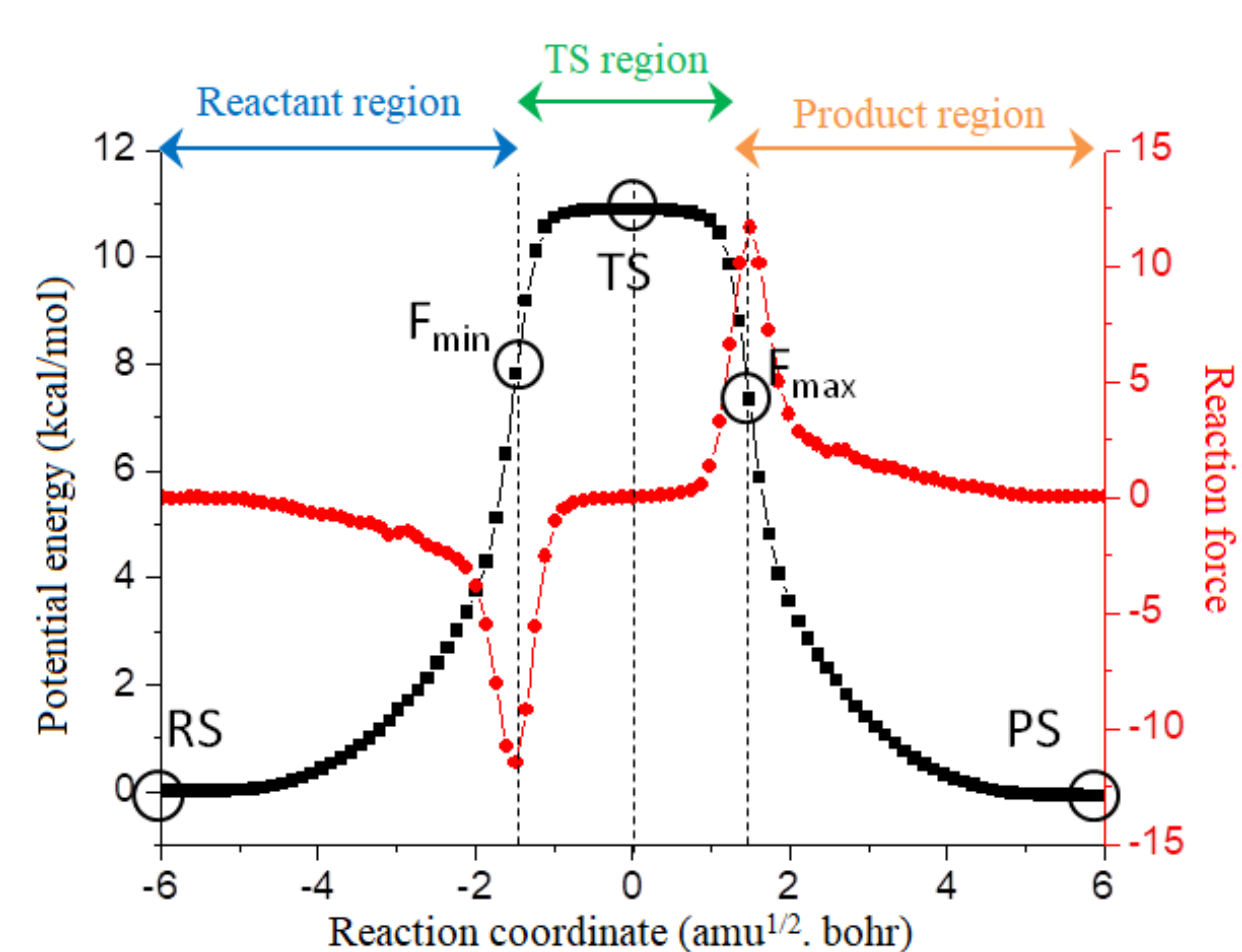


F _z conversion		
Gaussian	au	MV.cm ⁻¹
20	0.002	10.28
40	0.004	20.56
60	0.006	30.84
80	0.008	41.12
100	0.010	51.40

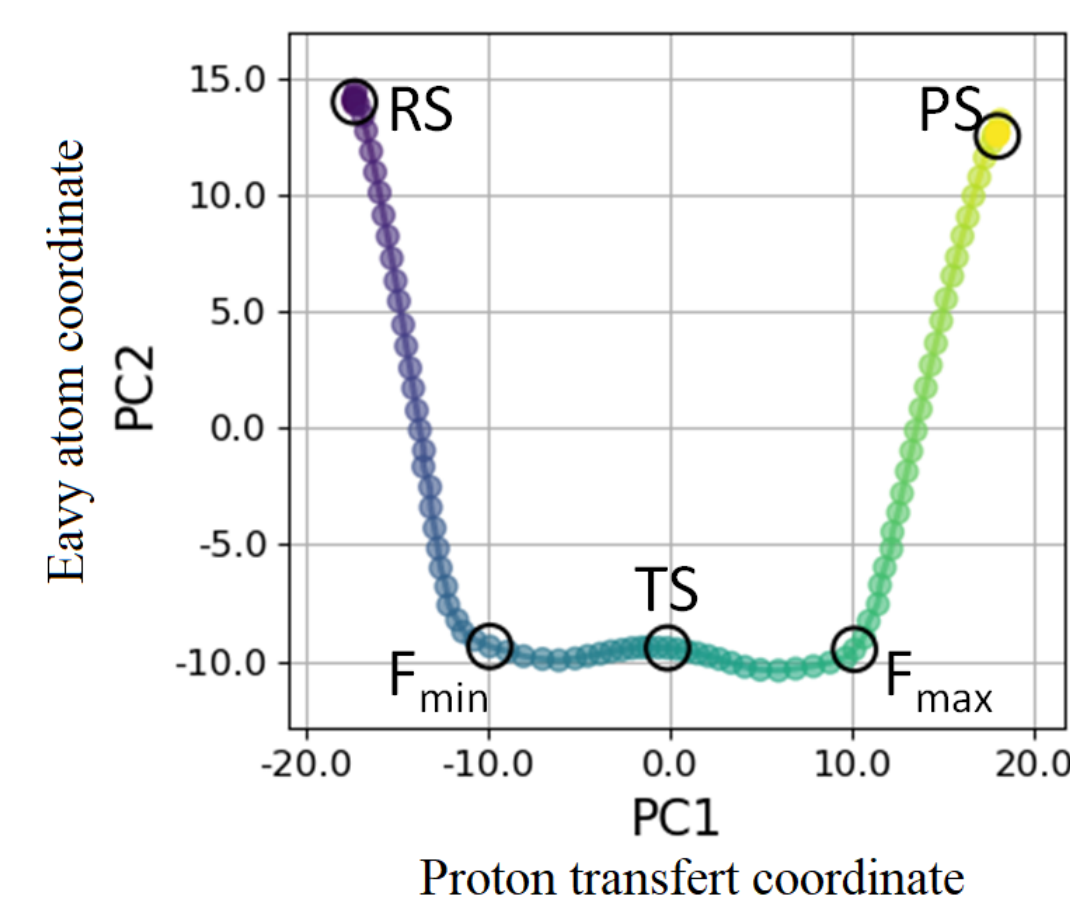
- DFT ω B97X-D/6-311++G(2d,2p) — Gaussian09
- ELF Topology — TopMod

3. Without electric field

- Potential energy profile : **Concerted mechanism**

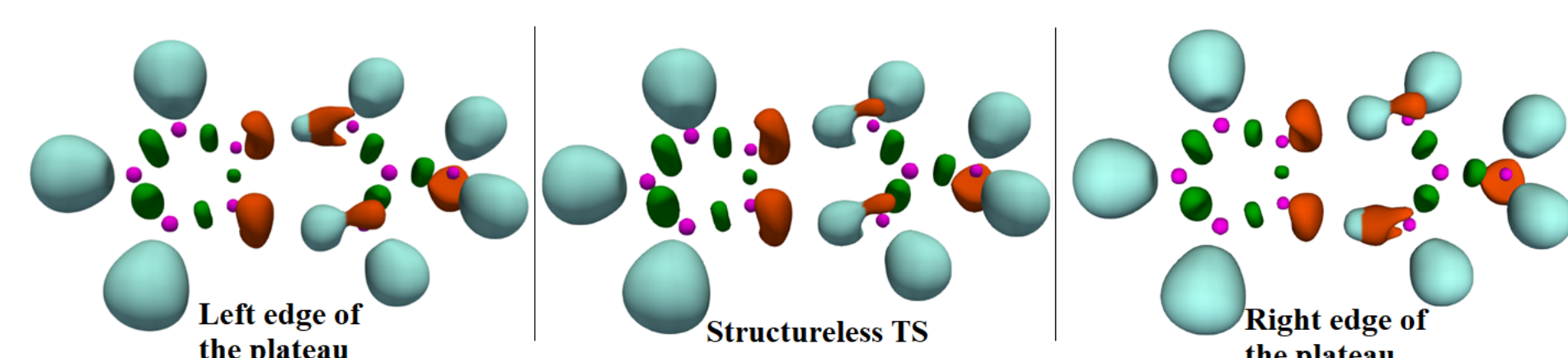
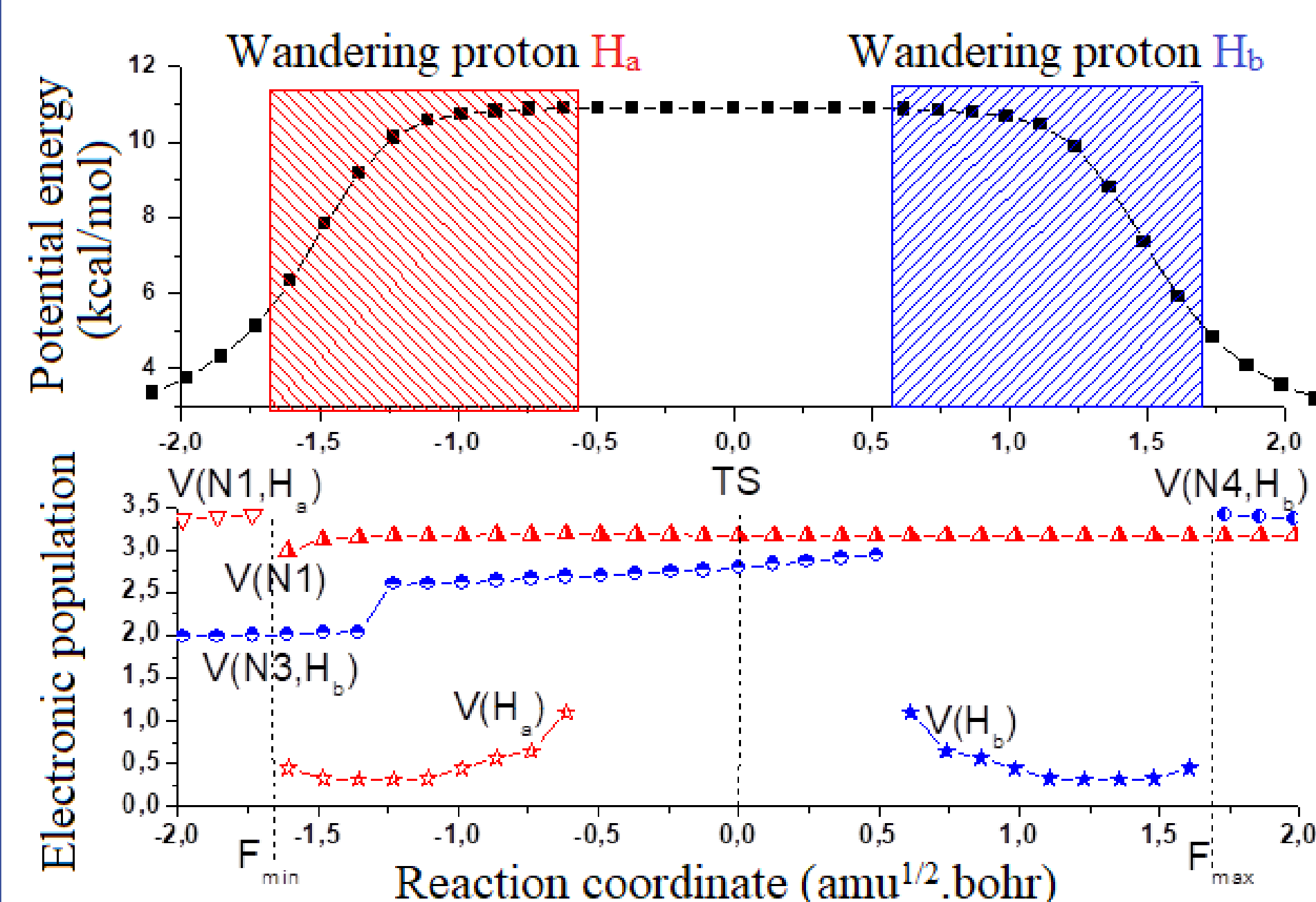


- ★ Principal component analysis of IRC structures



Both protons are transferred in the transition state region

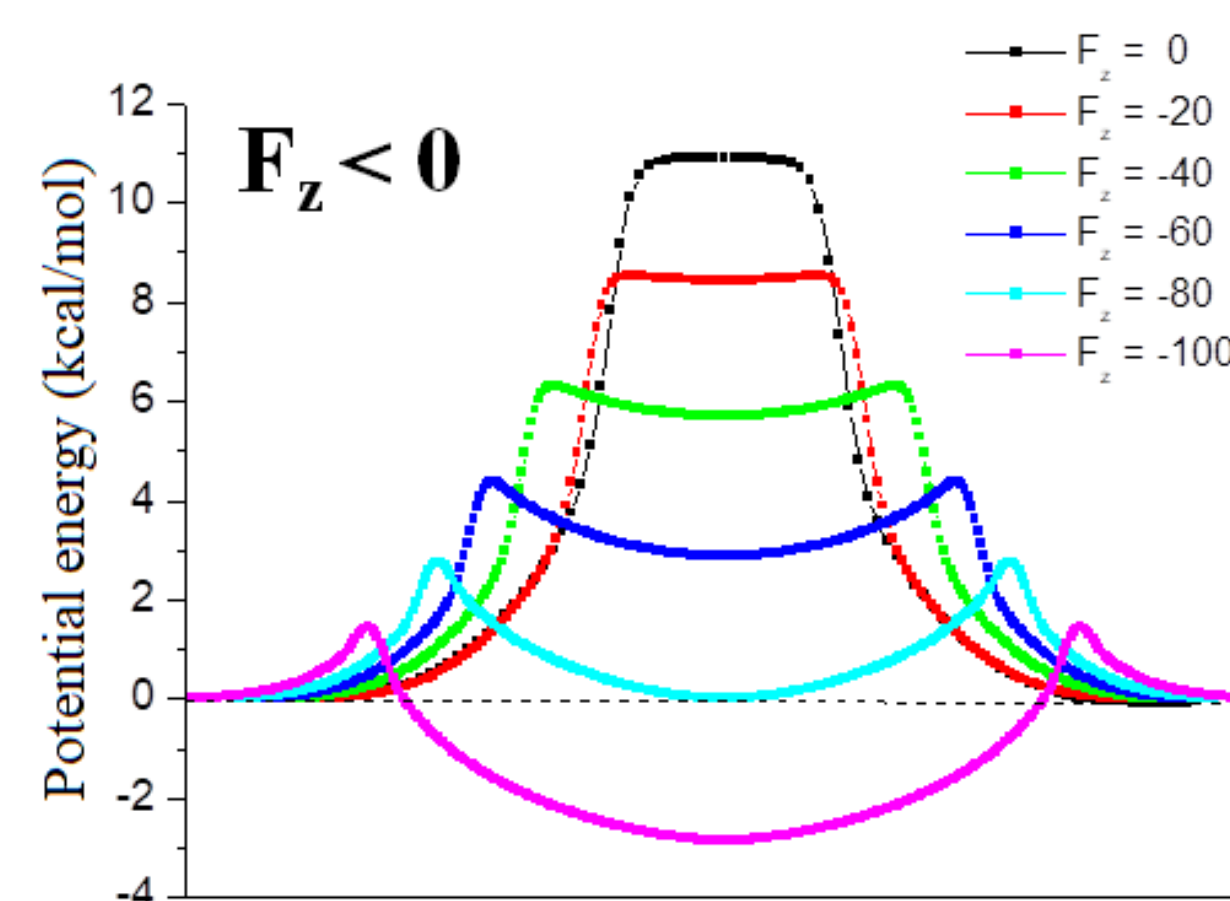
- ★ ELF Analysis along the reaction path



Proton transfer at the edge of the plateau
⇒ **Concerted asynchronous mechanism**

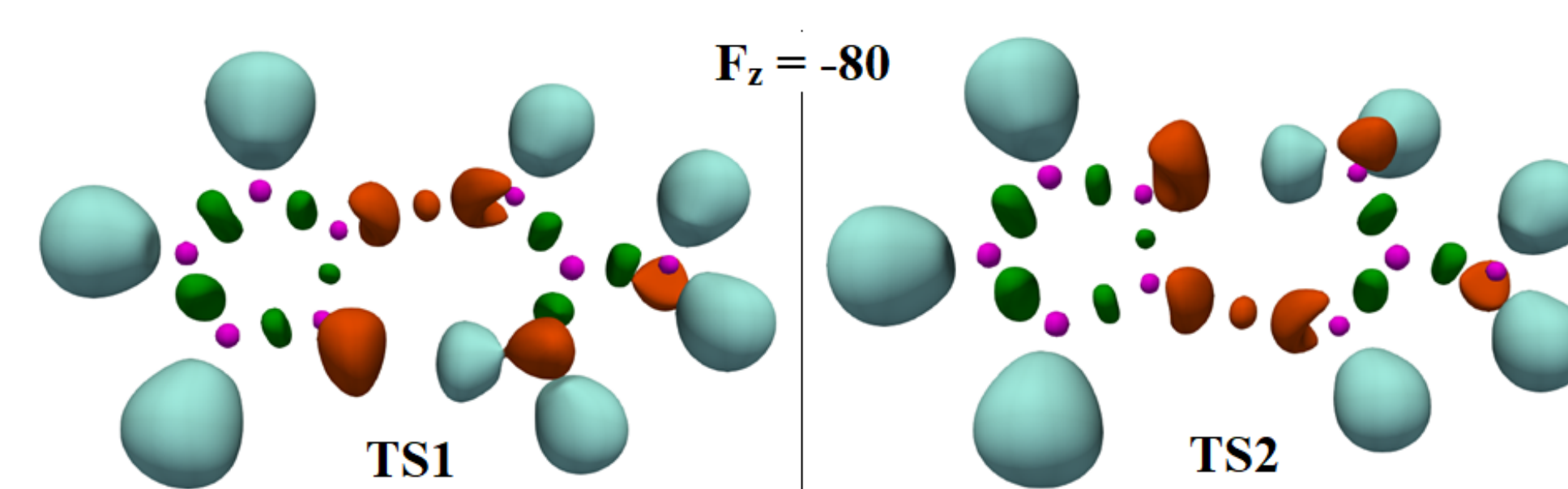
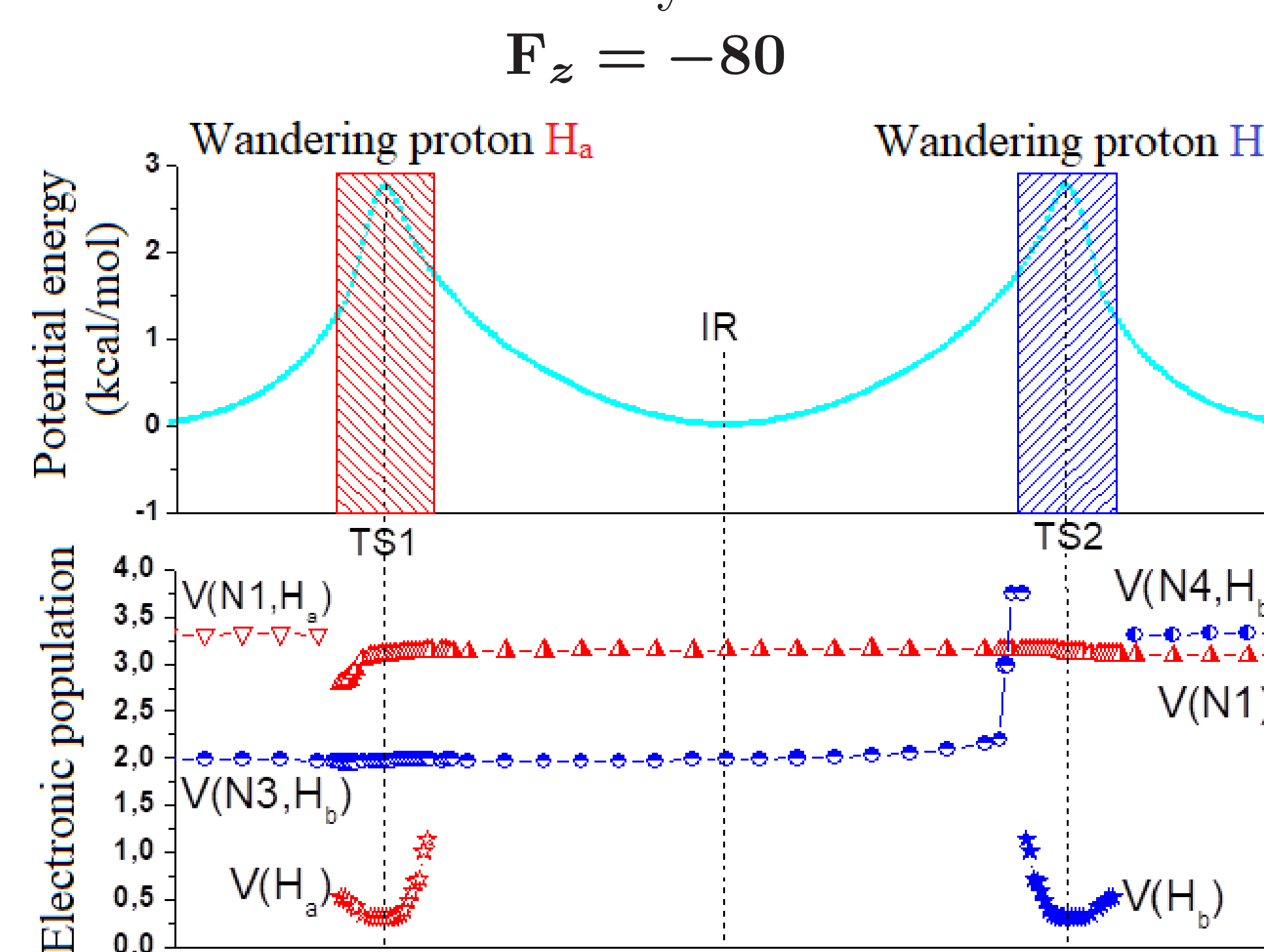
4. Effect of the Oriented External Electric Field

- Potential energy profile with electric field

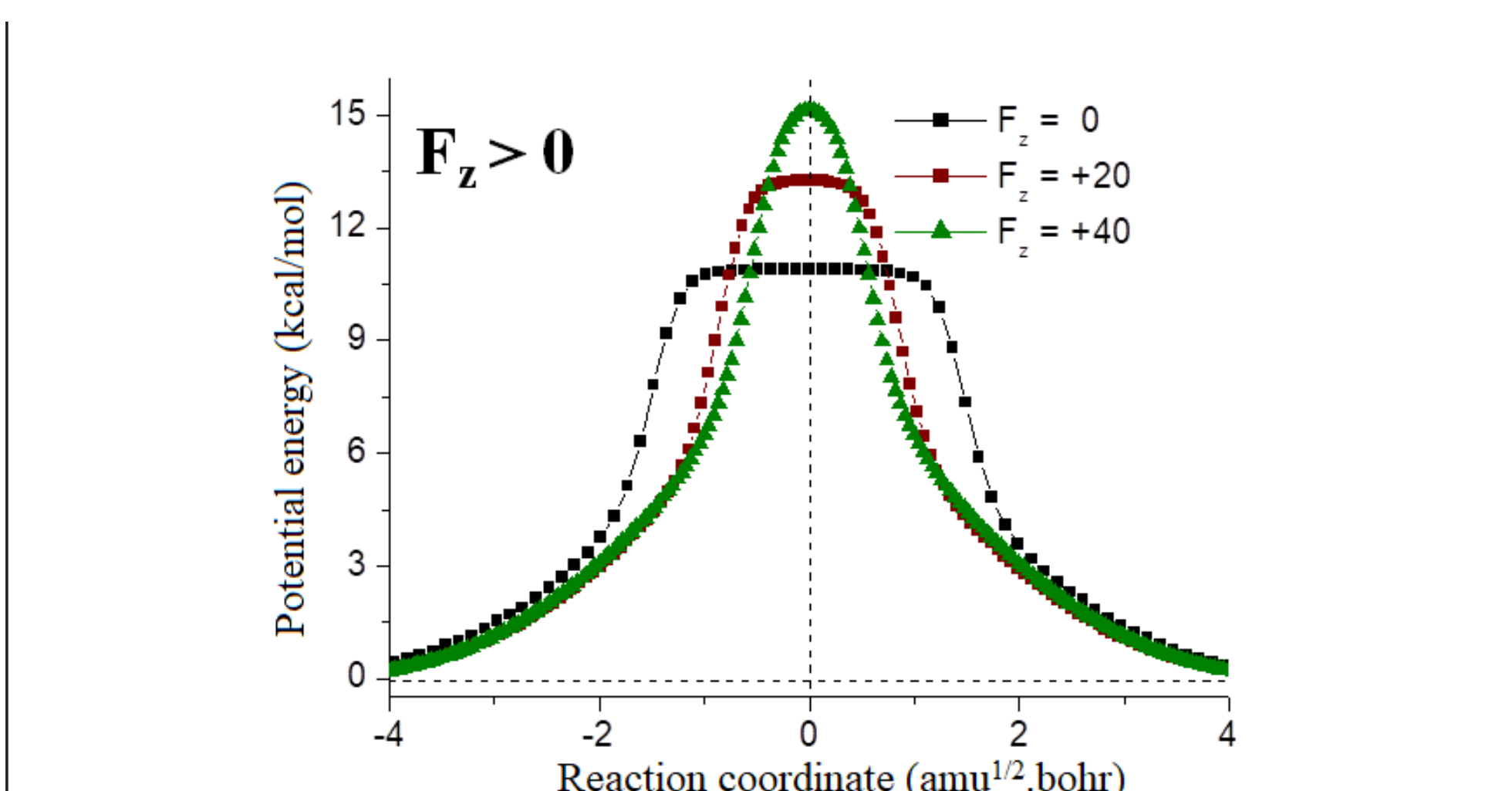


$F_z < -20 \Rightarrow$ Concerted $\rightarrow$ **Stepwise**

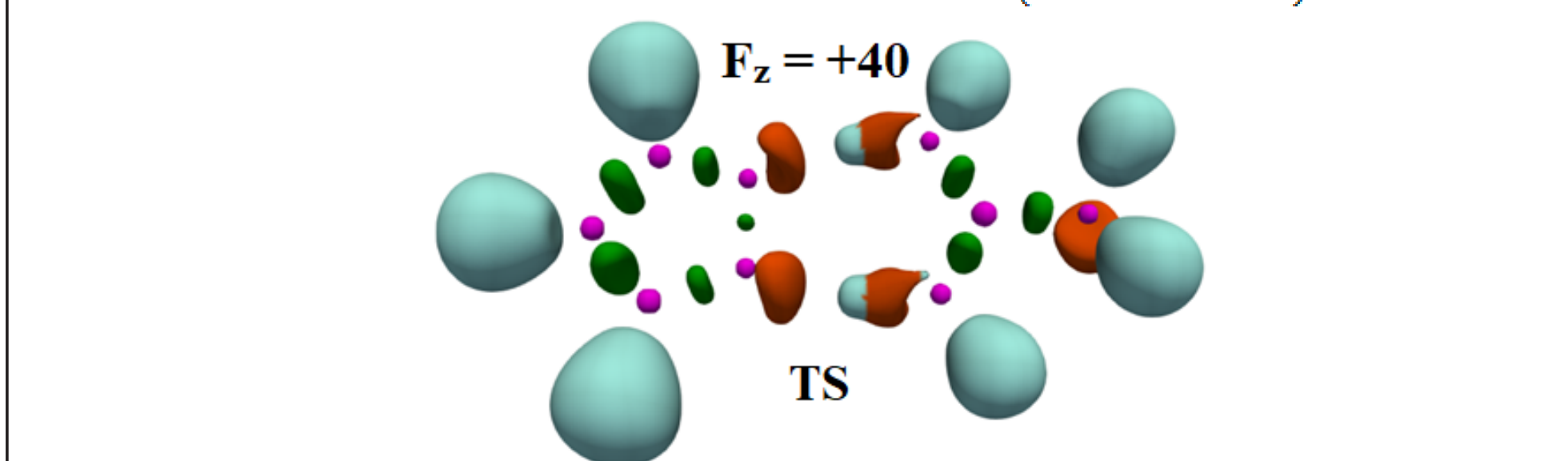
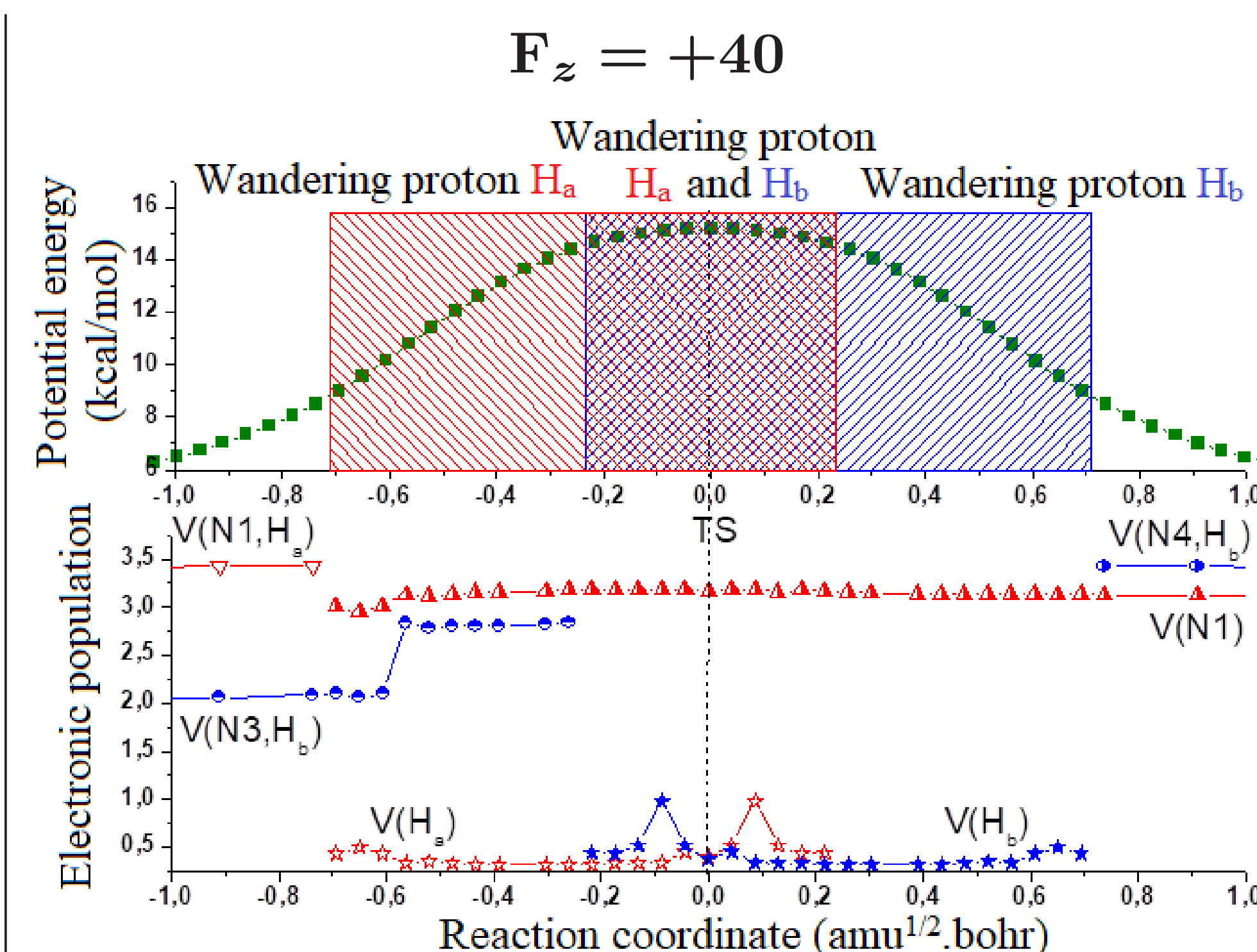
- ★ Bond Evolution Theory



$F_z < 0$, only one proton is delocalized at a time



$F_z > 0 \nearrow \Rightarrow$ Width of the plateau $\searrow$



$F_z = 40$, two wandering protons $\Rightarrow$ **Synchronous**

5. Conclusions

We have provided a detailed analysis of the effect of an OEEF on an atypical mechanism: the plateau reaction in the Pyrazole-Guanidine complex (**asynchronous concerted mechanism**). The electric field is a "smart reagent" that allows us to modulate the nature of the reaction mechanism to transfer protons **stepwise**, or in a **concerted synchronous** manner. It is a powerful tool for analyzing the arrangement of primitive processes in concerted mechanisms.

6. References

- [1] S. Shaik *et al.*, J. Am. Chem. Soc. **2021**, 142(29):12551 – 12562
- [2] A. Geoffroy-Neveux *et al.*, J. Phys. Chem. A **2022**, 126(20):3057–3071
- [3] G. Rauhut *et al.*, Phys. Chem. Chem. Phys. **2003**, 5(5):791 – 800