Virtual Reality Understanding of the Catalytic Mechanisms in SABRE

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Introduction

- **Goal:** To elucidate the para-hydrogen exchange mechanism in SABRE, esp. energetics, solvent's role, intermediates, etc. for $[Ir(H)_2(IMes)(py)_3]^+$
- **Pyridine** is chosen as the substrate, **methanol** the solvent

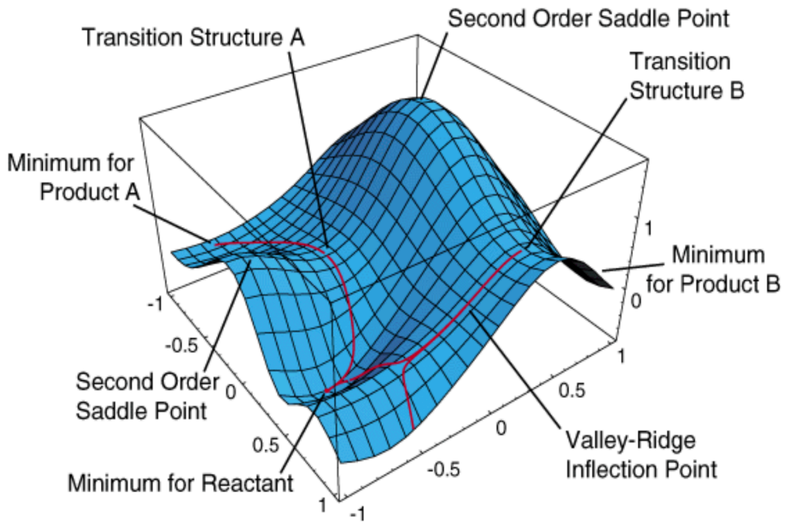
Methods

Ab initio electronic structure calculations

- **Code package:** FHI-aims
- **Level of theory:** PBE semi-local density functional + Tkatchenko-Scheffler term for van der Waals interactions
- **Basis sets:** Numeric Atom-Centered basis sets
- **Relativistic treatment:** Atomic ZORA
- **Convergence threshold:** 5×10^{-3} eV
- High numerical precision; uses all-electron calculations; computationally efficient

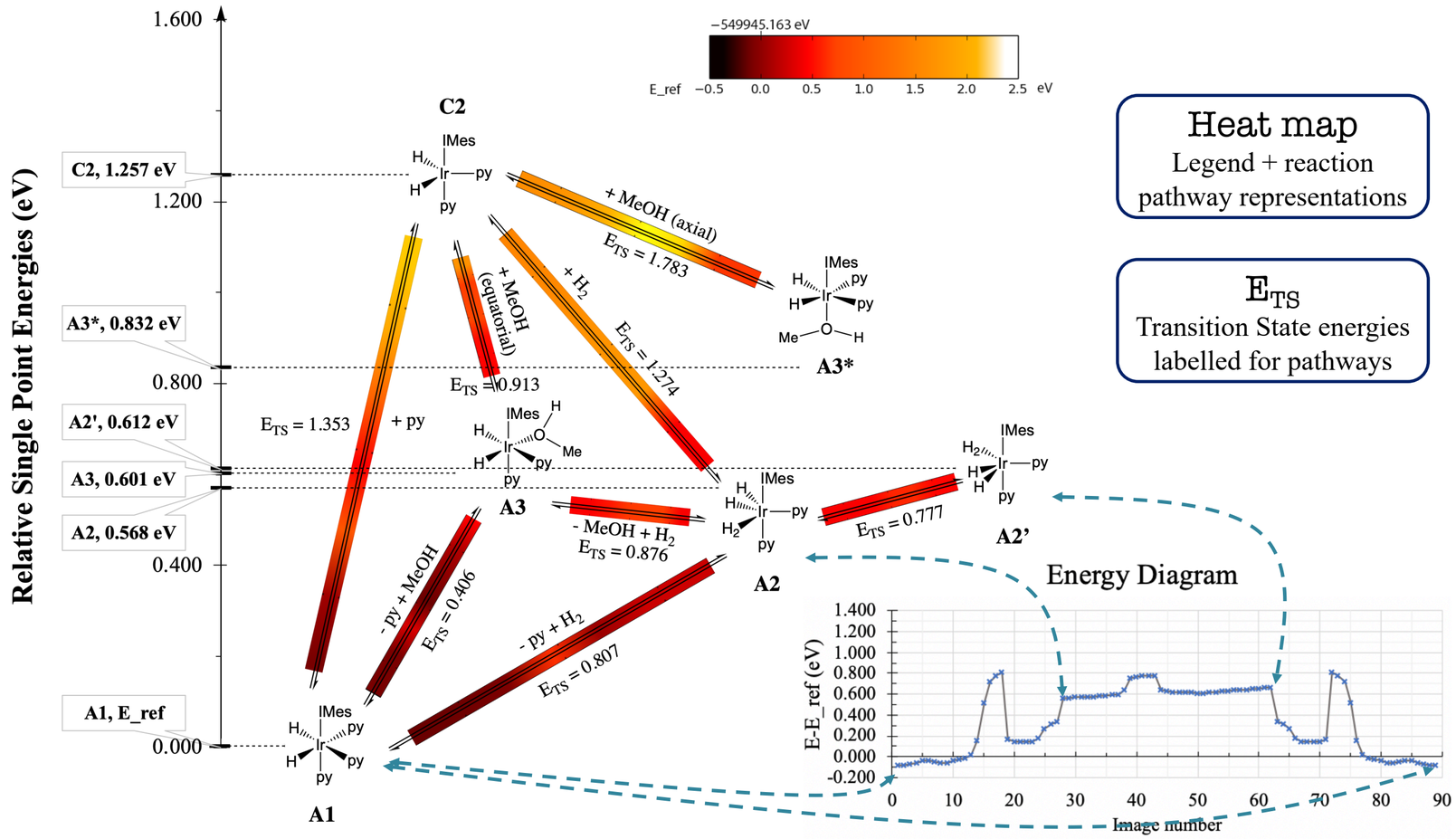
Potential Energy Surface probing algorithms

- **String method** for the minimum energy path (MEP)
- **Climbing Image technique** for approaching transition states accurately
- **Convergence threshold:** Maximum reside potential force of all images less than 0.01 eV/Å



Model potential energy surface. Schlegel, H.B., *J. Comput. Chem* **2003**, 24: 1514-1527.

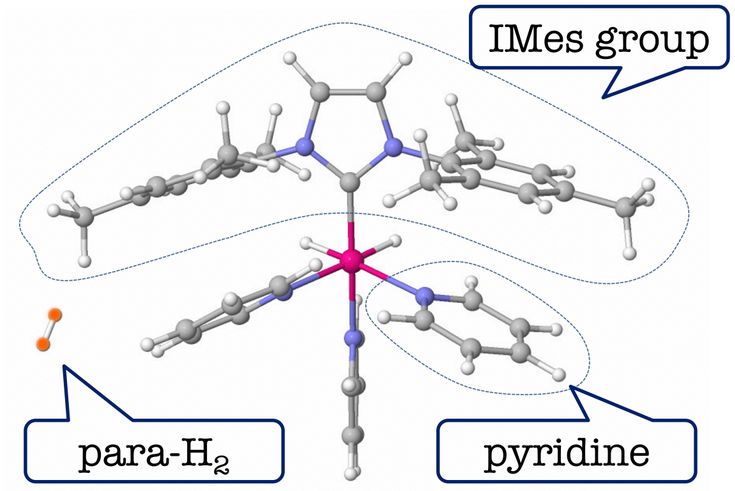
Reaction Network and Heat Map



Heat map
Legend + reaction pathway representations

E_{TS}
Transition State energies labelled for pathways

Key Pathway: para-H_2 refreshing



[Video] for the para-H_2 exchange animation, with energy diagram and heat map coloring.

[Virtual Reality Rendering] of the video

Conclusions

- **C2**'s existence as a stable intermediate species is **unlikely,** due to its high potential energy.
- **Dissociative interchange mechanism** (I_D) is dominating in this reaction network.
- **Solvent (methanol) assisted process** plays an important role in SABRE (through A3)
- This set of computation methods via FHI-aims has advantages of ***a)*** high numerical precision, ***b)*** using all-electron computation, ***c)*** yielding full reaction pathways.

References

[1] Blum, V.; et al. *Computer Physics Communications* **2009**, 180 (11), 2175-2196. [2] Cowley, M. J.; et al. *Journal of the American Chemical Society* **2011**, 133 (16), 6134-6137. [3] E, W.; Ren, W.; et al. *The Journal of Chemical Physics* **2007**, 126 (16), 164103. [4] Perdew, J. P.; et al. *Physical Review Letters* **1996**, 77 (18), 3865-3868. [5] Rayner, P. J.; et al. *Nature Communications* **2018**, 9 (1), 4251. [6] Theis, T.; et al. *Science advances* **2016**, 2 (3), e1501438.

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