Dynamics and Directionality: Mechanistic Studies from Excited-State Chemistry to ATPase Motors

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The speaker will present an overview of his research on the dynamics of photorearrangements, the hidden intermediate activation, and the mechanism of biomolecular motors. The photochemistry of the triplet di-π-methane rearrangement has been studied using computational methods, including high-level and DFT calculations.[1] With molecular dynamics,[2] the non-statistical nature in the dynamics was confirmed due to quasi-classical trajectories involving sequential formation and cleavage of bonds in the shallow triplet intermediate with lifetimes ranging from 13 to 1160 fs. Interestingly, substituent effects can destabilize the radical species on T_1 and the second triplet intermediate becomes the regioselectivity-determining step.[3] The reaction electronic flux (REF) method was used to assess the effect of aromaticity along the reaction coordinate. The REF could discriminate between π- and σ-bonds, suggesting the key role of aromaticity in the mechanism. Effects arising from triplet antiaromaticity alleviation and Baird's rule were also studied.[4] The presentation will then deal with research on full hidden intermediates, since these have been elusive to locate on a given potential energy surface (PES). Mainly, the focus has been on the E1cB/E2 borderline eliminations[5] and the Schmittel cyclization of enyne–allenes[6,7] as case studies. The electronic structure of these hidden species remains entirely uncoupled from the reaction coordinate. Therefore, we propagate forward and backward quasi-classical trajectories initialized in the transition state ensemble of the rate-determining step. The screening strategy considers that a few so-called 'hot' trajectories will eventually reach the full hidden intermediate,[6] higher in energy over the minimum energy path (MEP) connecting the reactant and product. Once this has been spotted, it is rationalized how the full hidden intermediate can be stabilized to be coupled to the reaction coordinate. Naturally, replacing a substituent in the reactant should change the landscape of the PES, although it is possible that PES's evolution could be studied systematically. Finally, recent studies on the mechanism of the F1-ATPase motor will be presented, on which a theory based on the single-molecule kinetics was developed that enabled to suggest an SN2-like nucleotide exchange.

[1] R. A. Matute, K. N. Houk, *Angew. Chem. Int. Ed.* **2012**, *51*, 13097. [2] G. Jimenez-Oses, P. Liu, R. A. Matute, K. N. Houk, *Angew. Chem. Int. Ed.* **2014**, *53*, 8664. [3] R. A. Matute, M. A. Garcia-Garibay, K. N. Houk, *Org. Lett.* **2014**, *16*, 5232. [4] R. A. Matute *et al.*, *J. Org. Chem.* **2018**, *83*, 5969-5974. [5] D. E. Ortega, R. Ormazabal-Toledo, R. Contreras, R. A. Matute, *Org. Biomol. Chem.* **2019**, *17*, 9874. [6] R. Duran, C. Barrales-Martinez, R. A. Matute, *Phys. Chem. Chem. Phys.* **2023**, *25*, 6050. [7] A. F. Flor-Lopez, R. A. Matute, P. Jaque, *Phys. Chem. Chem. Phys.* **2025**, *27*, 797.

Ricardo A. Matute earned his Ph.D. in Chemistry from the University of Chile in 2011, under the joint supervision of Profs. R. Contreras (University of Chile) and L. González (University of Vienna). He then completed postdoctoral research at UCLA, USC, and Caltech, working with Prof. K. N. Houk, and Nobel Laureates A. Warshel and R. A. Marcus. After five years in California, he returned to Chile in 2016. He is currently a faculty member at the Universidad Técnica Federico Santa María in Valparaíso.

His research focuses on theoretical and computational studies of photochemical reactions, photoredox catalysis, enzyme catalysis, and biomolecular motors.

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