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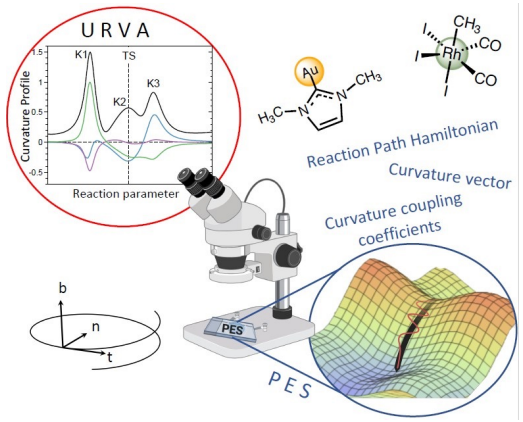
# Reaction mechanisms

## General concepts

### Unified Reaction Valley Approach

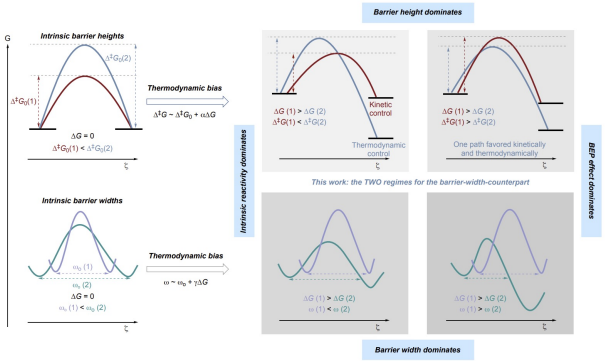
- URVA is a combination of vibrational spectroscopy and potential energy surface.
- The curvature of the reaction path is mapped by registering the changes in the normal vibrational modes. Each chemical reaction is characterised by a curvature profile in which maxima indicate important chemical events, that can be decomposed into internal coordinates components for a better understanding of the mechanism.




*Chem. Commun.* **2023**, *59*, 7151; image – *Catalysts* **2020**, *10*, 691, OA (CC BY license).

### Intrinsic Barrier Width

- Similar to Marcus' dissection of the barrier height, here the barrier width is separated into intrinsic barrier width and driving force effect on the barrier width. The distinct nature of the two components is proven.




- The effect of barrier width is evaluated *via* quantum mechanical tunnelling half-lives and the method is applied to conformational isomerisations of simple aromatic carboxylic acids.
- The main applications and test cases will be external electric field catalysis and strong vibronic coupling, in which it is possible to tune the barrier width.

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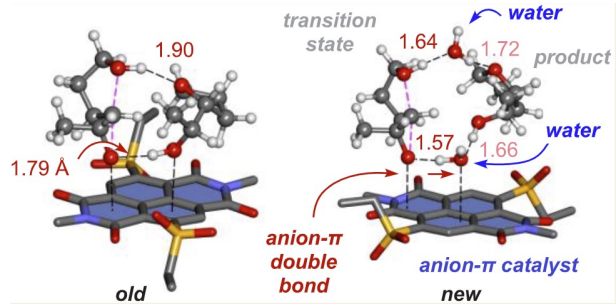
## New catalytic mechanisms

### Anion–π Autocatalysis

- The mechanism of anion-π autocatalysis, e.g., in the epoxide opening cyclization of ethers, has been long misunderstood.
- Computations at the B3LYP-D3/6-31+G*/PCM level of theory reveal a crucial role of the number of water molecules, which act as proton shuttles.
- Hydrogen bonded chains stabilise the charged transition featuring an anion-π double bond.

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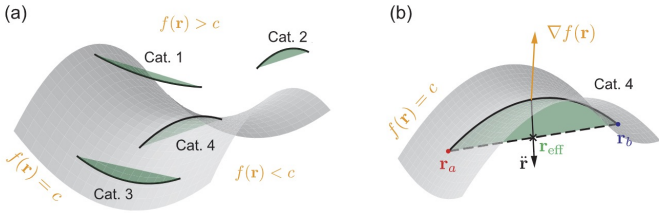
### Oscillation-Driven Catalysis

- Changing the environment rapidly can drive the catalyst away from the stationary states leading to anomalous performance.




- For example, an oscillatory voltage driven reaction occurs below the theoretical voltage, avoiding side reactions.
- This work presents a theoretical framework to study such catalytic systems using geometrical non-equilibrium theory to rapidly oscillate environments.
- Since a single free energy environment cannot be used to study the changing environment, a control-conjugated landscape encodes reaction kinetics.
- The method allows the design of oscillation-driven catalysts, beyond stationary theory, by using geometrical intuition.

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