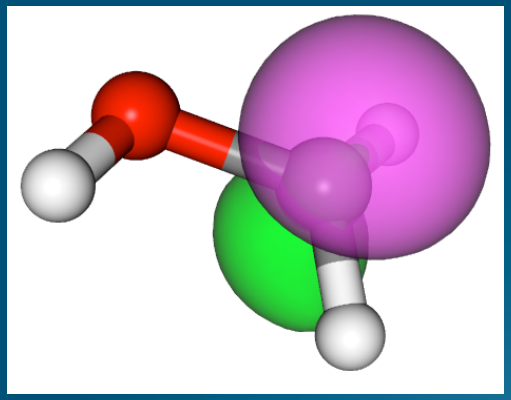
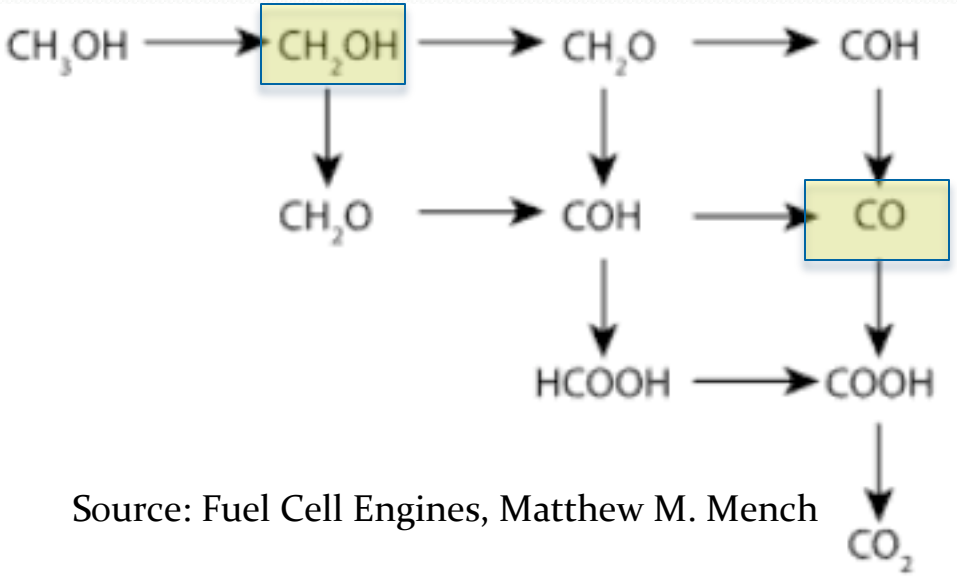
The influence of CO on the conical intersection of CH_2OH.



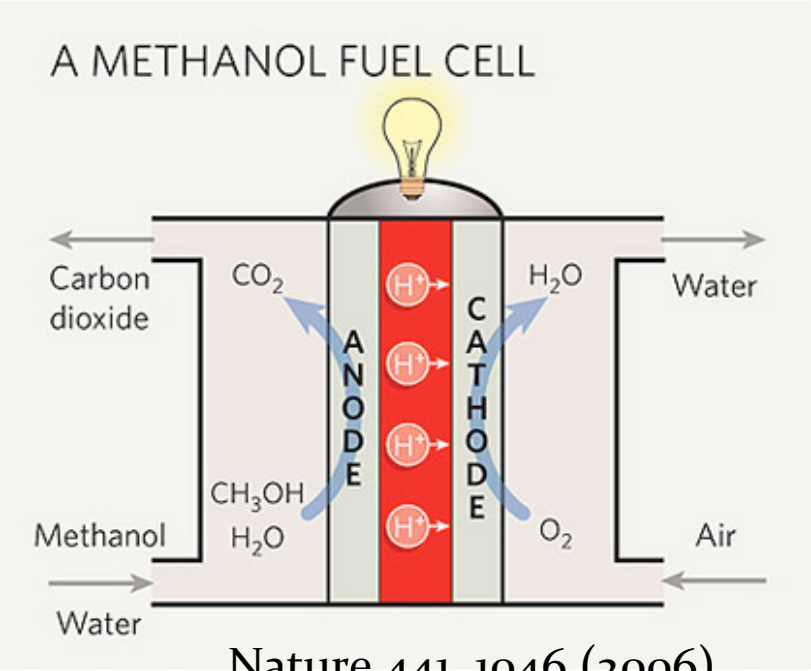
Johnson Agbo, *Sterling College*
Benj FitzPatrick, *University of Chicago*
Liam Jacobson, *University of Utah*
Aaron Pierpont, *University of North Texas*
Luis Rivera, *Texas A & M University*
Lorena Tribe, *Penn State Berks*

Relevance

- Direct Methanol fuel cell.
- CO can be a poison in a fuel cell.
- CH_3OH and its dissociation products play an important role in combustion chemistry.
- Can we bias the pathway to reduce CO?



Source: Fuel Cell Engines, Matthew M. Mench



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Conical Intersections

- Nonadiabatic effects play an important role in many areas of physics and chemistry. One such effect is the presence of conical intersectons that couple electronic states.
- Conical intersections can provide an efficient pathway for radiationless decay between electronic states, which can often lead to products having very different velocity distributions.
- Are excited state processes at conical intersections sensitive to the influence of a polar and polarizable environment?

Experimental grounding

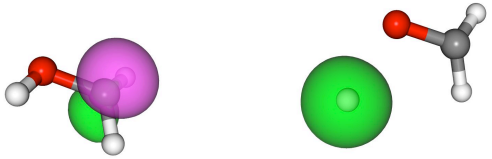
Goals of experiment:

- Measure velocities of dissociated hydrogen atoms
- Determine ratio of D/H coming off of R-OD/R-OH

- Procedure
  - Create $CD_2OH\cdots CO$ ions with an electrospray nozzle.
  - Select ion of interest using a quadrupole mass filter.
  - Use a laser to knock the extra electron off and another to electronically excite the molecules.
  - Ionize the products and measure their velocities.
  - Isotopic substitution

Methods

- Geometry Optimization:
  - Complete active space SCF (CASSCF)
    - Can calculate multiple states necessary for describing electronic states that are close in energy.
    - Which orbitals should be included?*



- Accurate Energetics
  - Multireference configuration interaction (MRCI)
  - CASPT2 (CASSCF + 2nd-order PT)
    - Gives more accurate energies due to included dynamical electron correlation
    - Locating Conical Intersections
    - Lagrange multiplier methods
    - Newton-Raphson

*CASSCF/6-311G(d,p)

Dynamics on the potential energy surface

- Classical trajectories on the ab initio surface.
- Wave packet dynamics.
- Questions to address:
  - Does the trajectory even get close to the conical intersection?
  - Do the calculations and experiment agree?
  - Is the conical intersection located at a place that is accessible by the excited state?

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