# Ligated silver hydride nanoclusters for hydrogen storage and catalysis





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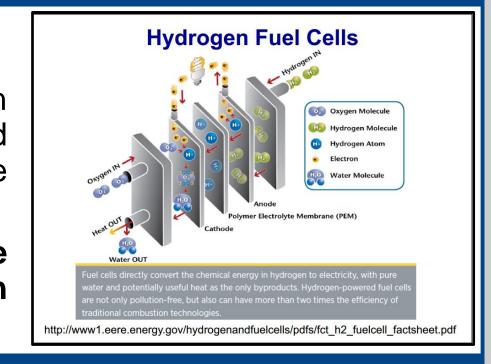
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#### I. Hydrogen Storage

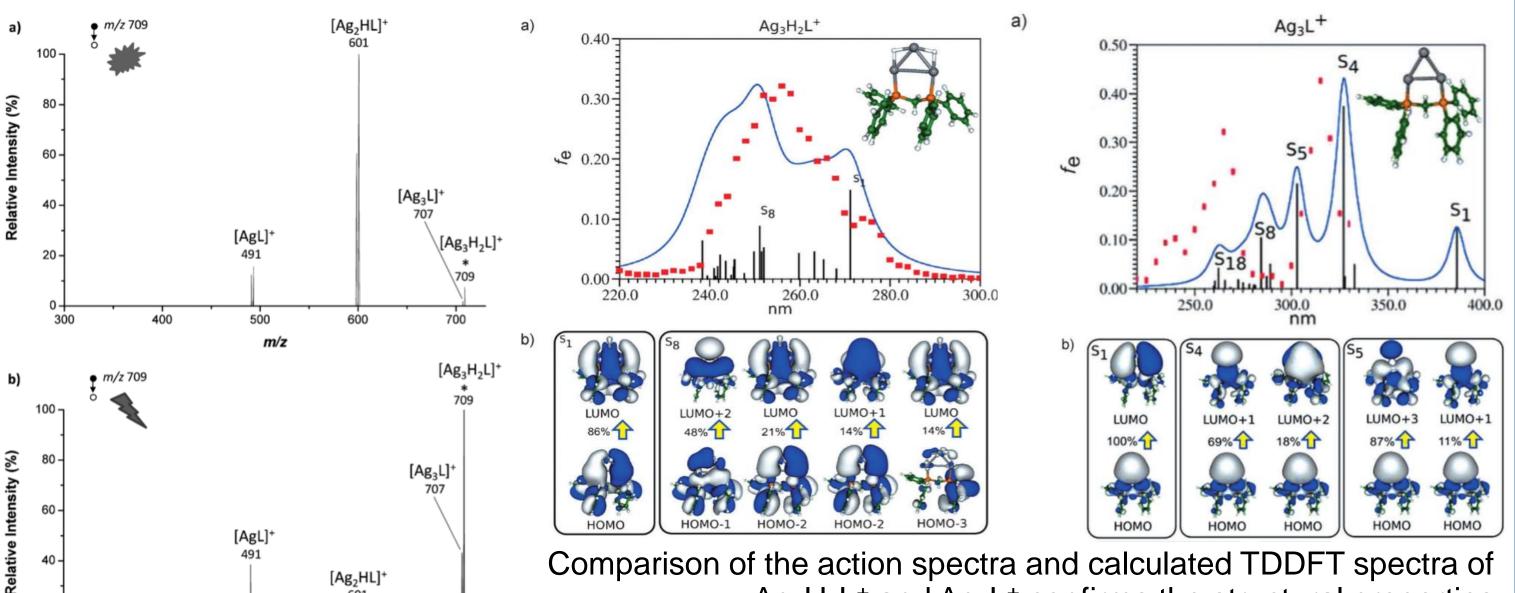
#### Motivation

While transition metal hydrides are unlikely to be used as hydrogen storage materials due to their low H% weight content, there is continued interest in the use of transition metal compounds to catalyze the decomposition of other compounds with higher H% weight content.<sup>[1]</sup>

Therefore, we investigate metal hydrids as a hydrogen storage medium in which hydrogen can be released by heating or irradiation with light.<sup>[2,3]</sup>

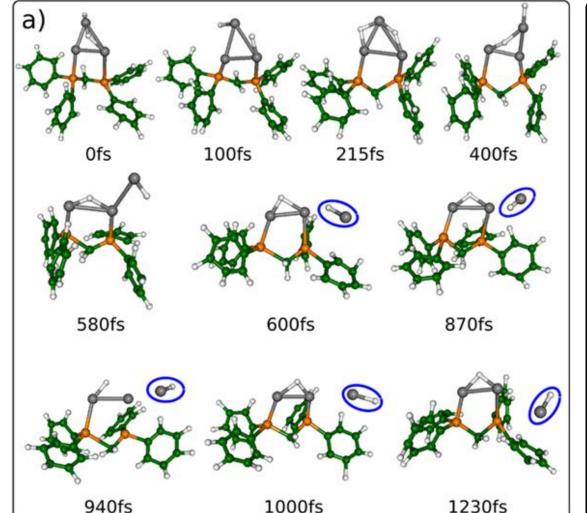


# Theoretical and Experimental Results MS Spectra and Spectral Characterization of Structures



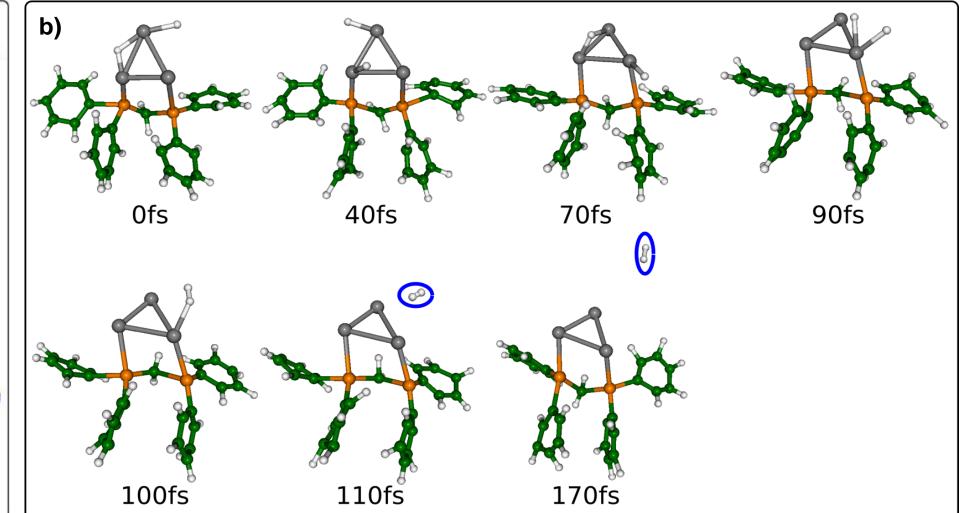
Ag<sub>3</sub>H<sub>2</sub>L<sup>+</sup> and Ag<sub>3</sub>L<sup>+</sup> confirms the structural properties MS spectra showing the fragmentation of the [Ag<sub>3</sub>H<sub>2</sub>L]<sup>+</sup> ion under conditions of: a) collision-induced dissociation (CID), b) laser-induced dissociation (LID) at 260 nm

### AgH and Hydrogen Release in the Ground State S<sub>0</sub> and Excited State S<sub>1</sub>



release of AgH is favourable.

 $\frac{1}{940 \text{fs}}$   $\frac{1}{1000 \text{fs}}$   $\frac{1}{1230 \text{fs}}$   $\frac{1}{1230 \text{fs}}$  Snapshots of the MD "on the fly" in the ground state  $S_0$  showing that



Snapshots of the MD "on the fly" in the excited state  $S_1$  illustrating that the release of hydrogen is favourable.

 The reason for photo-release of hydrogen is the difference between the geometry in ground and excited states of complex.

# **Summary and Outlook**

- This finding may be a general route for the photo-release of hydrogen in ligated metallic hydrides which can be used as a hydrogen storage medium where hydrogen can be released by irradiation with light.
- Photo-activation leads to excitation within the Ag<sub>3</sub>H<sub>2</sub> core involving a geometry change, which weakens the silver-hydrogen bonds allowing for hydrogen release.
- Stabilization of the metal cluster by the ligands may favour hydrogen release.
- Choice of ligand plays a crucial role as it will be shown in this poster by examining the decomposition of the promising storage material formic acid catalyzed by ligated silver nanoclusters.

# Theoretical and Experimental Methods

- structural and optical properties: DFT and TD-DFT with B3LYP functional and def2-TZVP AO basis set
- Stuttgart relativistic effective core potential (RECP) with corresponding AO basis set for silver atoms
- absorption spectra: TD-DFT with B3LYP functional and TZVP AO basis set or PBE0 functional and TZVP AO basis set
- IR spectra form vibrational analysis
- MD "on the fly": RI-PBE with def2-TZVP AO basis set
- Multistage mass spectrometry in combination with ion-molecule reaction, collision-induced dissociation (CID) and laser-induced dissociation (LID)
- UV action spectroscopy for photo-fragmentation spectra

#### References

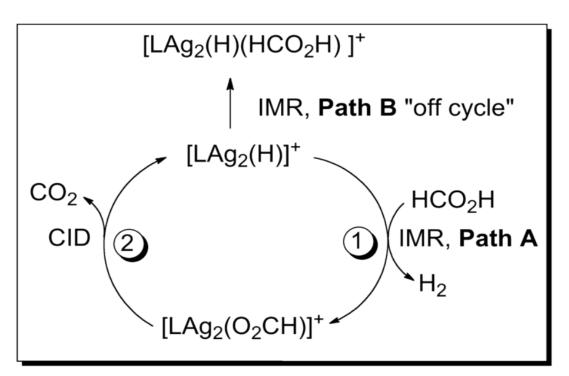
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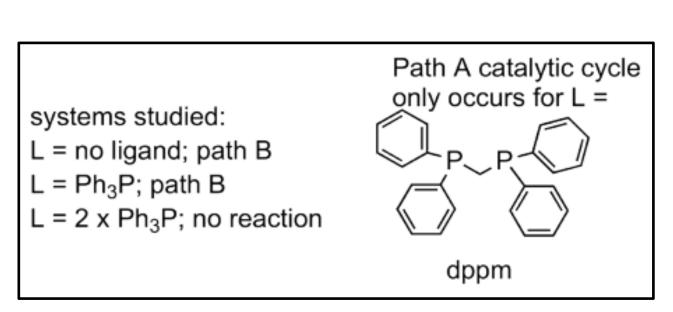
# II. Concept of Synergistic Role of Ligand and Substrate in the Selective Decarboxylation of Formic Acid Catalyzed by Binuclear Silver Hydride Cations

Motivation

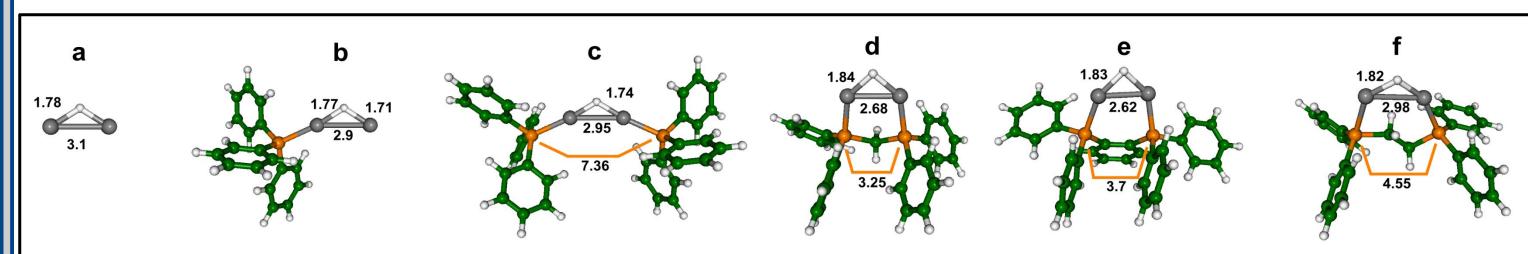
The decomposition of formic acid is one of the most widely studied topics in chemistry, with a rich history of more than a century. The selective, catalyzed decomposition of formic acid has potentially important applications in areas ranging from hydrogen storage<sup>[4]</sup> through to the generation of an in-situ hydrogenation source for reduction of organic substrates. The latter reaction may prove useful in the production of key platform chemicals from biorenewable resources.

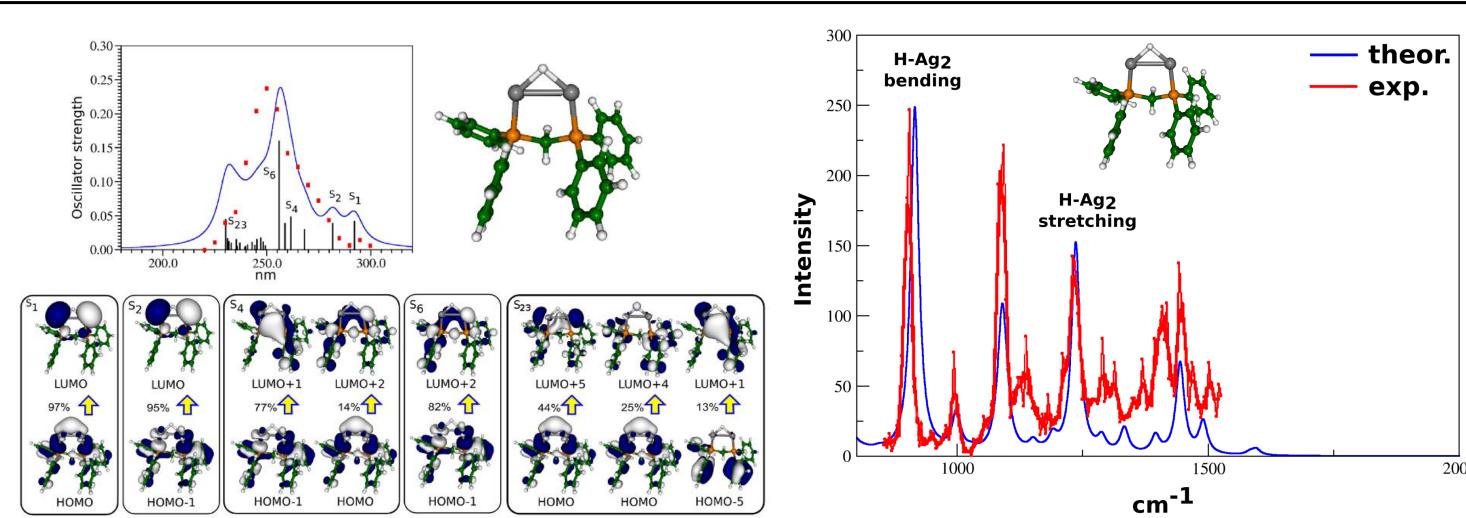
This motivated us to examine the role of ligands in promoting decomposition of formic acid catalyzed by the binuclear silver hydride cations,<sup>[5]</sup> [LAg<sub>2</sub>(H)]<sup>+</sup> for six systems as shown bellow.





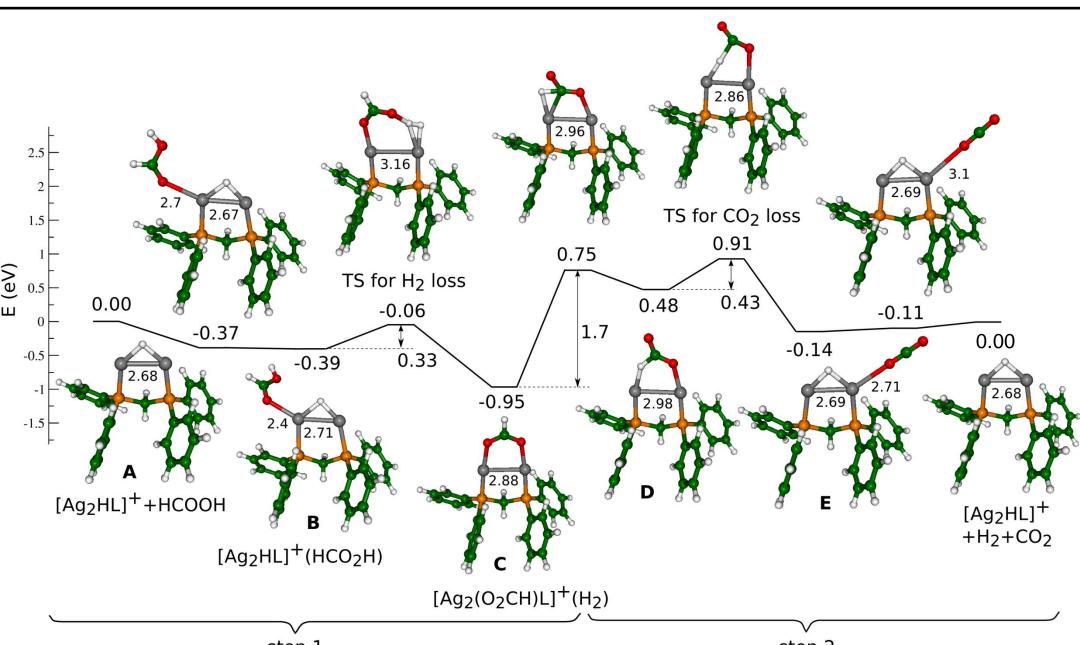
## Results: 1. DFT Determined Structures and Spectroscopical Confirmation





Agreement between action spectrum and TD-DFT calculated absorption, as well as between IR experimental and theoretical spectra confirm structural properties.

# 2. DFT Calculated Energy Profile Provides Mechanism of Catalytic Cycle

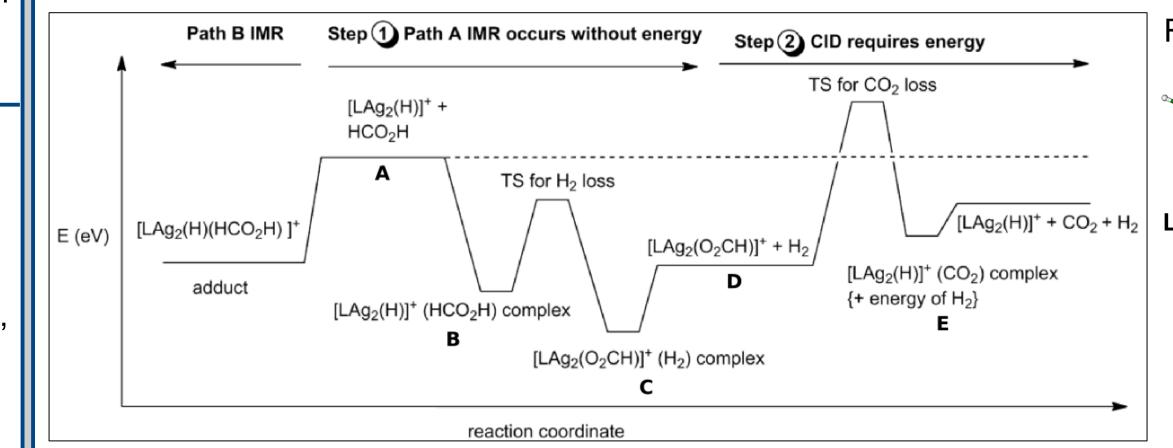


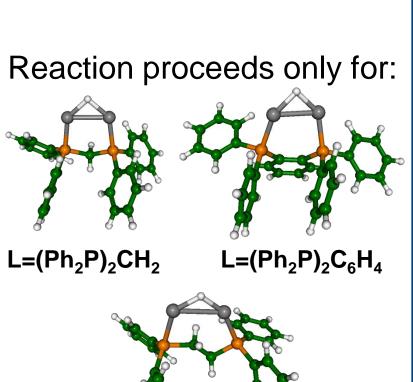
This involves two steps.

- **Step 1:** The ion-molecule reaction of formic acid with [LAg<sub>2</sub>H]<sup>+</sup> to produce [LAg<sub>2</sub>(O<sub>2</sub>CH)]<sup>+</sup> is exothermic with L=((Ph<sub>2</sub>P)<sub>2</sub>CH<sub>2</sub>).
- Oxygen binds to Ag weakening Ag-H bond and make it available for H<sub>2</sub> formation which is exothermic by 0.95 eV
   For this purpose the subunit Ag<sub>2</sub>P<sub>2</sub> with positive charge must remain intact which is dependent on ligand; for L with CH<sub>2</sub> and C<sub>6</sub>H<sub>4</sub> this is the case.
- Step 2: The mechanism for CO<sub>2</sub> release involves breaking of Ag-O bond, formation of Ag-H-C bond,
- overcoming the barrier for formation of CO<sub>2</sub> necessary for its release
   Catalytic cycle involving release of H<sub>2</sub> and CO<sub>2</sub> can occur experimentally since CID is involved for release of CO<sub>2</sub> due to temperature conditions allowing to overcome the barrier

#### **Summary and Outlook**

- Hydrogen loss is mediated by ligands; without ligand no reaction;
- Catalytic cycle is dependent on choice of the ligand:
- only for ligands preserving intact Ag<sub>2</sub>P<sub>2</sub> subunit reaction proceeds
- Design of efficient catalyst using ligated silver hydrids based on understanding of synergistic role of ligand and substrate





 $L=(Ph_2P)_2(CH_2)_2$