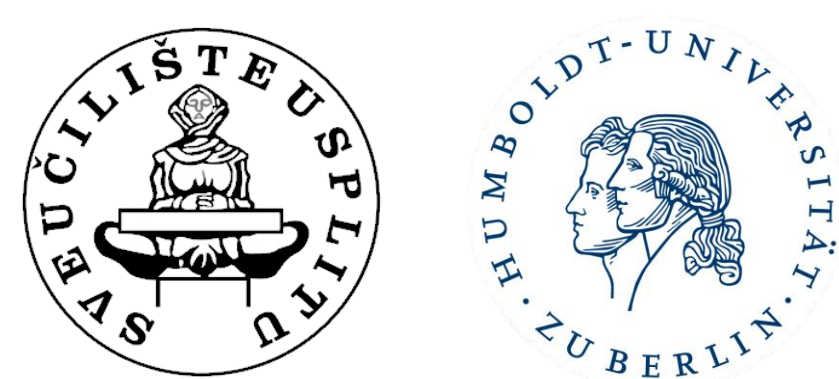


Ligated silver hydride nanoclusters for hydrogen storage and catalysis



Marjan Krstić^a, Vlasta Bonačić-Koutecký^{a,b}

Marion Girod^c, Rodolphe Antoine^d, Luke MacAleese^d, Jérôme Lemoine^c,
Athanasios Zavras^e, George N. Khairallah^e, Philippe Dugourd^d, and Richard A. J. O'Hair^e



^a Interdisciplinary Center for Advanced Science and Technology (ICAST) and
Center of Excellence for Science and Technology – Integration of Mediterranean region (STIM), University of Split, Meštrovićevo Šetalište 45, 21000 Split, Croatia

^b Department of Chemistry, Humboldt-University Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

^c Institut des Sciences Analytiques, Université Lyon 1, CNRS UMR 5280 Lyon, France

^d Institut Lumière Matière, Université Lyon 1, CNRS UMR 5306, Lyon, France

^e School of Chemistry, University of Melbourne, Victoria, Australia

Université Claude Bernard Lyon 1

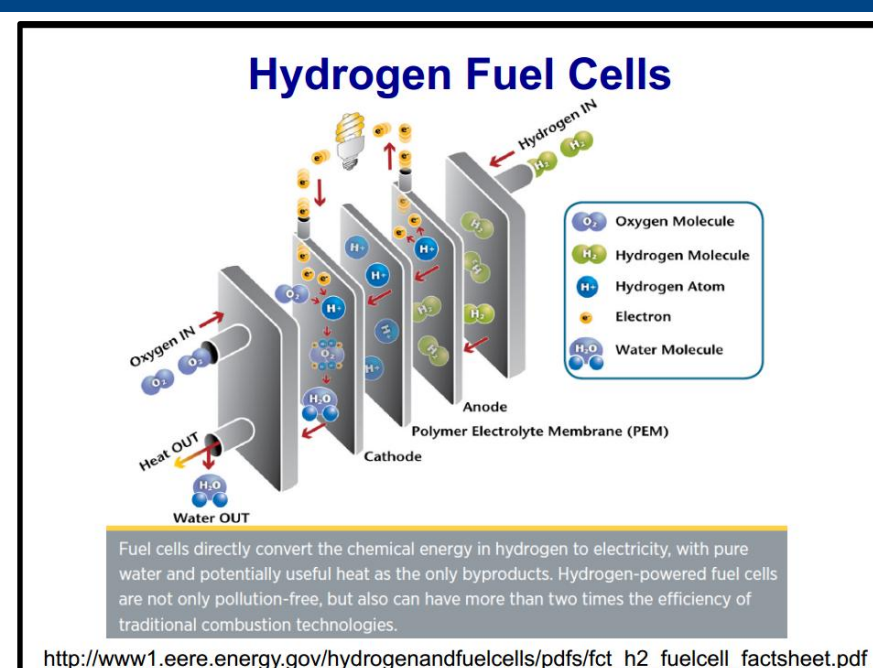


I. Hydrogen Storage

Motivation

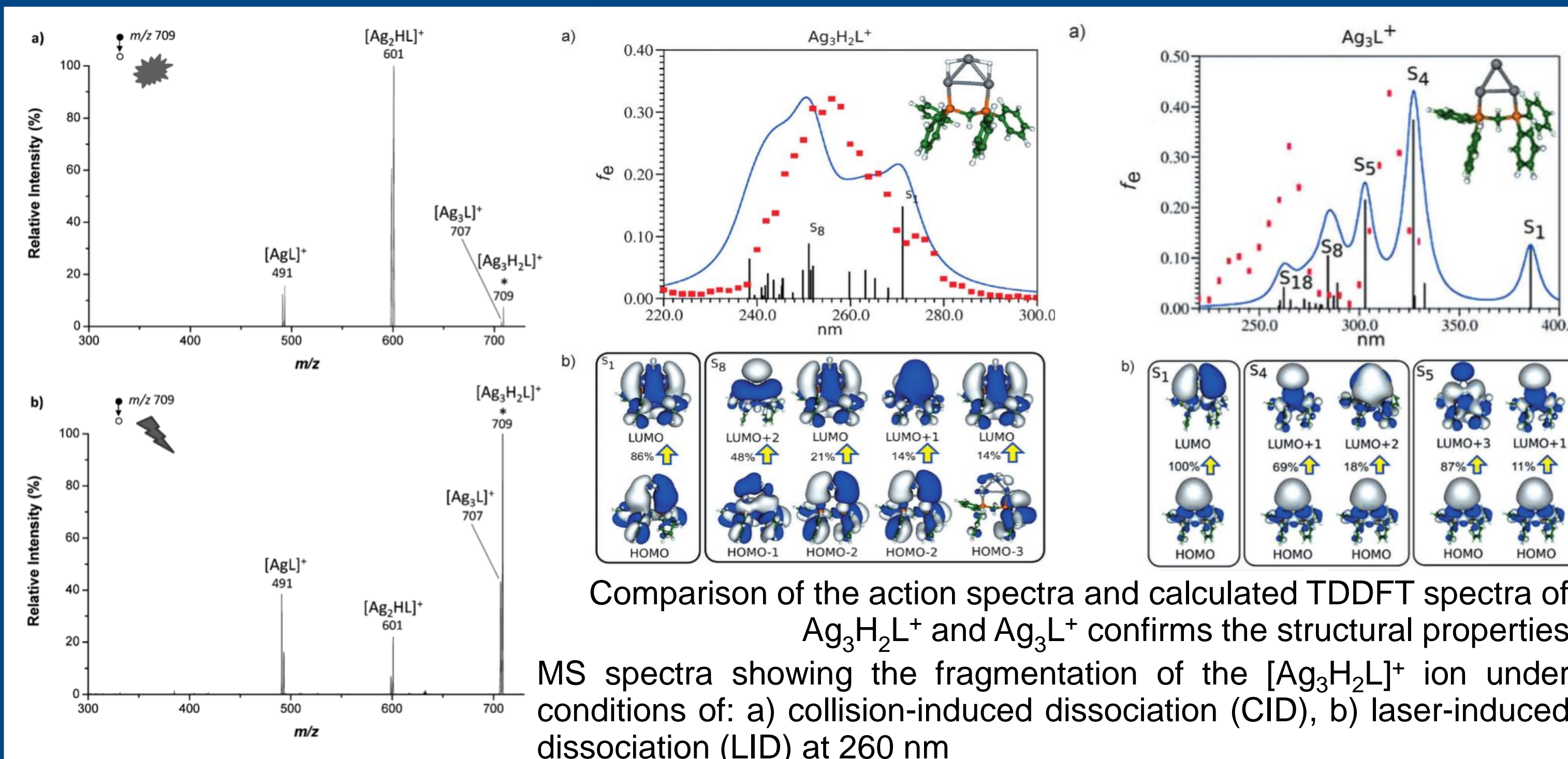
While transition metal hydrides are unlikely to be used as hydrogen storage materials due to their low H% weight content, there is continued interest in the use of transition metal compounds to catalyze the decomposition of other compounds with higher H% weight content.^[1]

Therefore, we investigate metal hydrides as a hydrogen storage medium in which hydrogen can be released by heating or irradiation with light.^[2,3]

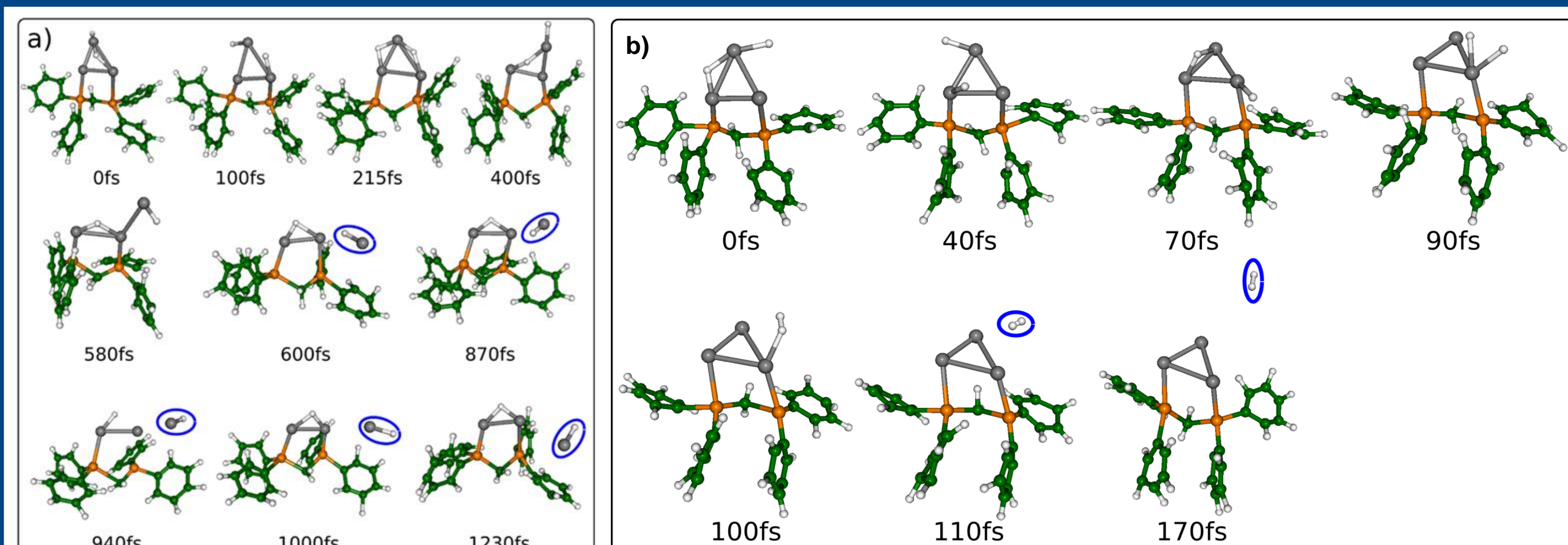


Theoretical and Experimental Results

MS Spectra and Spectral Characterization of Structures



AgH and Hydrogen Release in the Ground State S_0 and Excited State S_1



- 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_3H_2 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 from 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

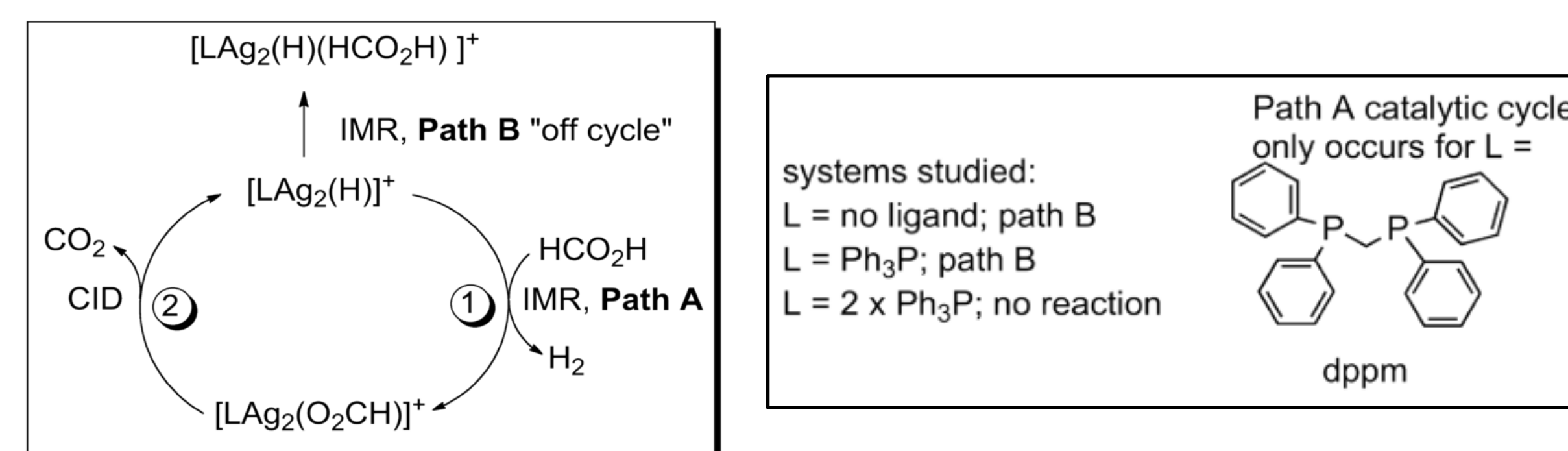
- [1] W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283
- [2] M. Girod, M. Krstić, R. Antoine, L. MacAleese, J. Lemoine, A. Zavras, G. N. Khairallah, V. Bonačić-Koutecký, Ph. Dugourd, R. A. J. O'Hair, *Chem. Eur. J.* **2014**, *20*, 16626
- [3] S. Daly, M. Krstić, A. Giuliani, R. Antoine, L. Nahon, A. Zavras, G. N. Khairallah, V. Bonačić-Koutecký, Ph. Dugourd, R. A. J. O'Hair, *PCCP*, **2015**, DOI:10.1039/c5cp01160d
- [4] G. N. Khairallah, R. A. J. O'Hair, *Int. J. Mass Spectrom.* **2006**, *254*, 145
- [5] A. Zavras, M. Krstić, G. N. Khairallah, M. Girod, S. Daly, R. Antoine, Ph. Maitre, V. Bonačić-Koutecký, Ph. Dugourd, R. A. J. O'Hair, "The role of the ligand in the selective decarboxylation of formic acid catalyzed by binuclear silver hydride cations", in preparation

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

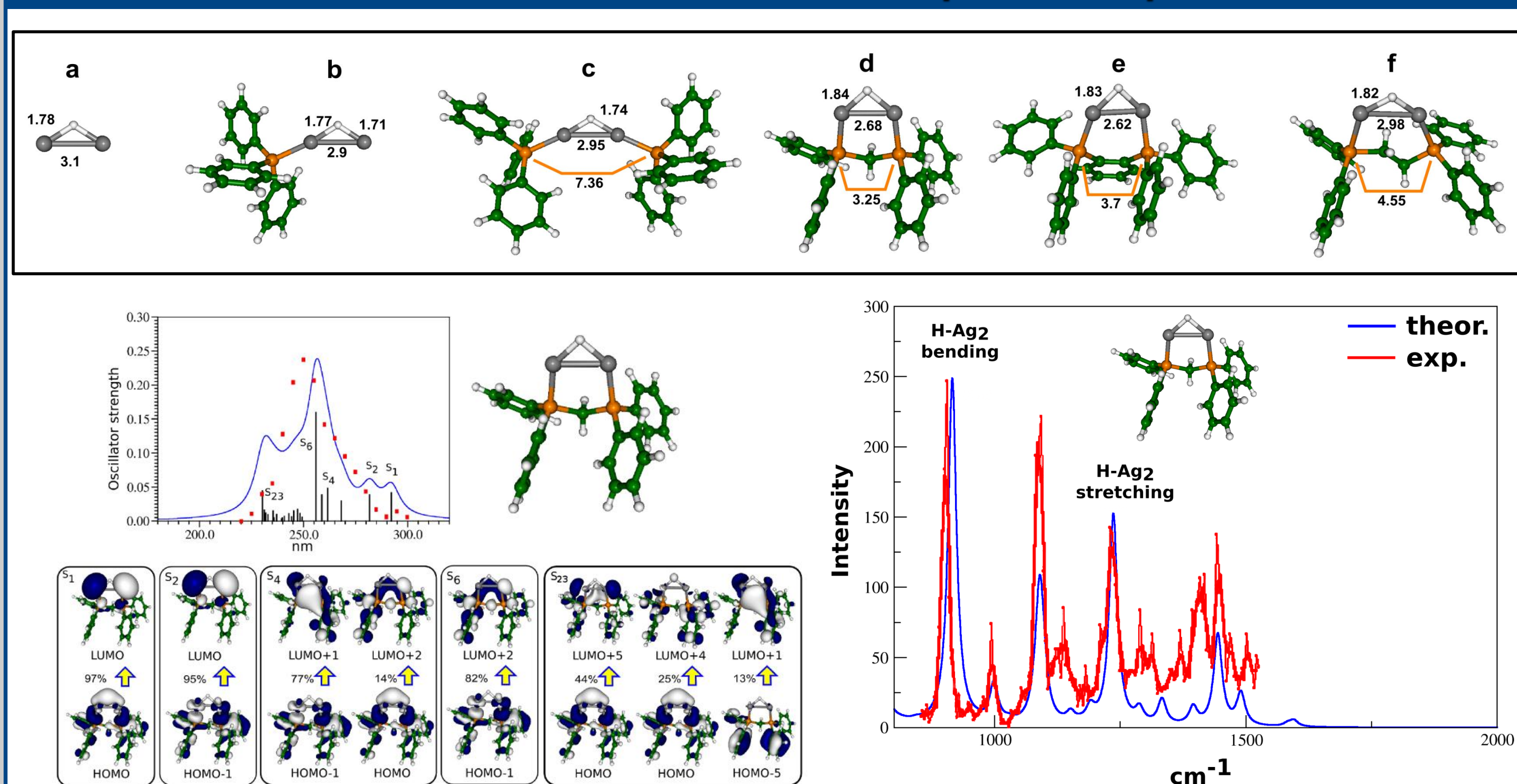
Motivation

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^[4] 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.

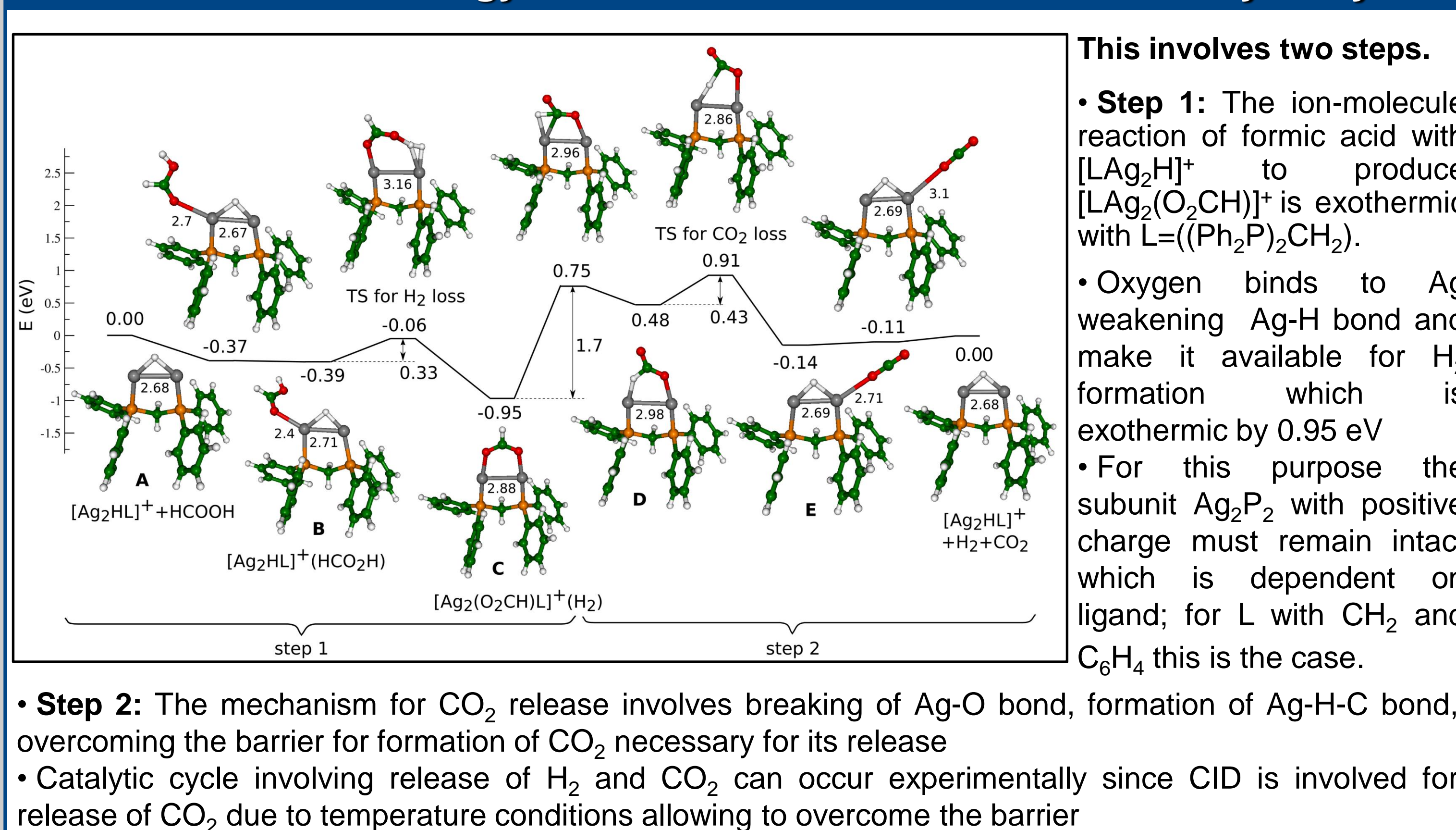
This motivated us to examine the role of ligands in promoting decomposition of formic acid catalyzed by the binuclear silver hydride cations,^[5] $[LAG_2(H)]^+$ for six systems as shown below.



Results: 1. DFT Determined Structures and Spectroscopical Confirmation



2. DFT Calculated Energy Profile Provides Mechanism of Catalytic Cycle



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_2P_2 subunit reaction proceeds
- Design of efficient catalyst using ligated silver hydrides based on understanding of synergistic role of ligand and substrate

