Swiss Photochemistry Symposium 2022 June 17, 2022

Ultrafast Two-Dimensional Infrared Spectroscopy of Transition Metal Hydrides: Couplings, Solvation and Proton-Coupled Electron Transfer

R. J. Fernández-Terán,[1,2*] J. Ruf,[2] A. Dimitrieva,[2] and J. A. Weinstein[1]

[1] Department of Chemistry, University of Sheffield. Sheffield, S3 7HF, United Kingdom
[2] Department of Chemistry, University of Zurich. CH-8057 Zurich, Switzerland.
(Ricardo.Fernandez@sheffield.ac.uk)

Transition metal hydrides (TMH) are ubiquitous intermediates in many chemical and catalytic transformations, and can also be involved in proton-coupled electron transfer (PCET).[1,2] Despite their importance, their vibrational dynamics have been largely unexplored.

Using 2D-IR spectroscopy, we have recently shown that the M–H and M(C≡O) stretching modes become strongly coupled and delocalized—thus enhancing the weaker M-H mode—only when the hydride and CO ligands are in a trans configuration.[3] We exploited this enhancement to monitor the ultrafast solvation dynamics of the hydride ligand in aprotic solvents of varying polarities and viscosities. We observe a non-monotonic change in the amplitude of a long-lived inhomogeneous component vs. solvent basicity/acidity (**Fig. 1A**). We thus hypothesize that the hydride ligand acts as a molecular "*Dr. Jekyll and Mr. Hyde*"—manifesting a more hydridic or acidic character according to the nature of the solvent (**Fig. 1B**). When protic alcohols of differing acidity are added as co-solvents, we observe an increase in the amplitude of this long-lived solvation component, proportional to the amount of alcohol (**Fig. 1C**). Finally, using 2D-IR spectroelectrochemistry, we show that the protonation and oxidation state of the metal can be unambiguously determined, allowing us to monitor PCET reactions directly from the hydride perspective. In addition, we are able to monitor directly the differences in solvation of the cationic and neutral species, which play a crucial role in the transfer of the 2nd electron and subsequent PCET.

Altogether, these results illustrate—from a fundamental, microscopic and ultrafast perspective—how the nature of the solvent and solute–solvent interactions are intrinsically linked to the PCET reactivity of these complexes, opening future avenues towards its control.

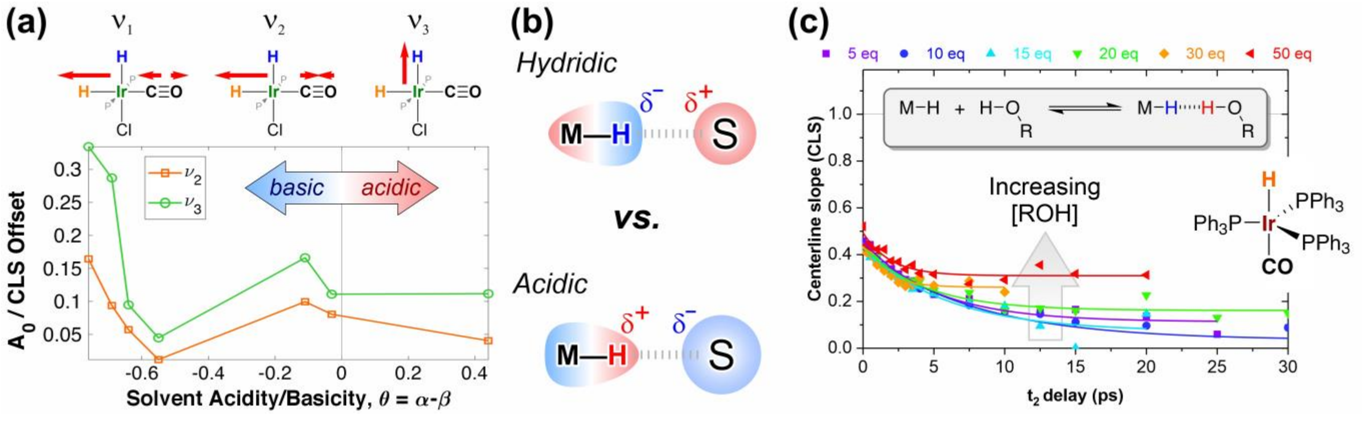

Figure 1: (***A***) Solvation dynamics of [Ir(H)$_2$(CO)(PPh$_3$)$_2$Cl] in aprotic solvents; (***B***) Hydridic/acidic character of a TMH; (***C***) Solvation dynamics of [HIr(CO)(PPh$_3$)$_3$] with fluorinated alcohols.

[1] T. Liu et al., *Nat. Chem.* **2018**, *10*, 81 87
[2] T. Liu et al., *J. Am. Chem. Soc.* **2019**, *141*, 17245–59
[3] R. Fernández-Terán et al., *Inorg. Chem.* **2020**, *59*, 7721–26.