

Ultrafast Dynamics of Ir(III) Hydrides: Is Time-resolved Infrared Spectroscopy a Viable Technique for Monitoring M-H Stretching Modes?

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THINK AND DO THE EXTRAORDINARY

Motivation

Transition metal hydrides are an important class of molecules used in many photocatalytic reactions and as materials for energy storage.

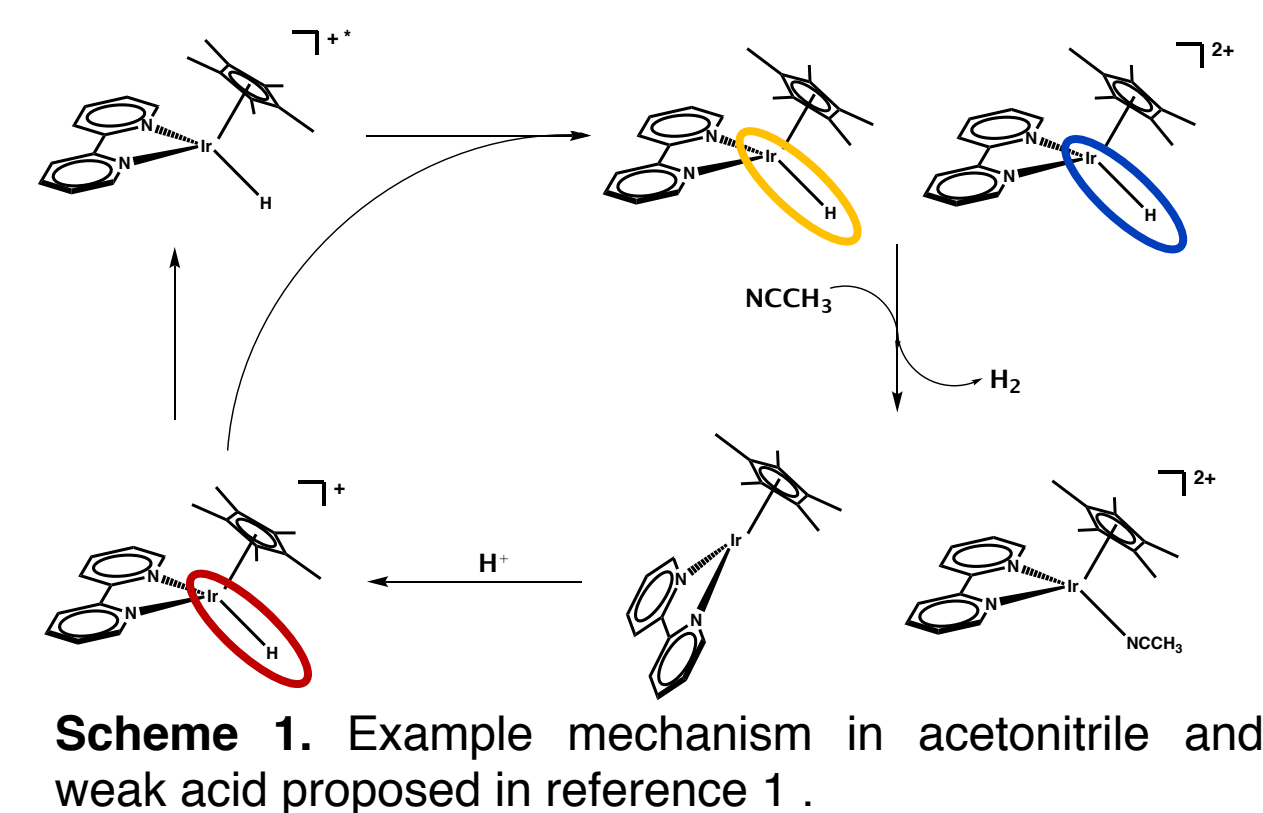
Sensitive time-resolved techniques can be used to study the short-lived excited states and photoproducts of these molecules.

Transient infrared (TRIR) spectroscopy is a valuable method for monitoring the changes in structure of molecules upon light excitation.

No one had ever observed metal-hydride (M-H) bond stretching modes using TRIR due to low IR absorbance of these modes.

By utilizing a *robust* transition metal hydride and sensitive equipment, perhaps M-H stretching modes could be observed using TRIR, opening the door to future work with more reactive metal hydrides?

Why Ultrafast TRIR Spectroscopy?



[IrCp*(bpy)H]⁺ is a highly photoactive molecule that is known to produce H₂ in the presence of light, acetonitrile, and weak acid.¹ Ultrafast transient absorption (UFTA) spectroscopy of the complex in methanol suggest the presence of intermediates during deprotonation but broad electronic transitions are difficult to use in making assignments. Vibrational spectroscopy, such as FTIR, supplies structural information that would easily identify the presence of possible intermediates. However, weak IR stretching modes make TRIR experiments of metal hydrides rather difficult.

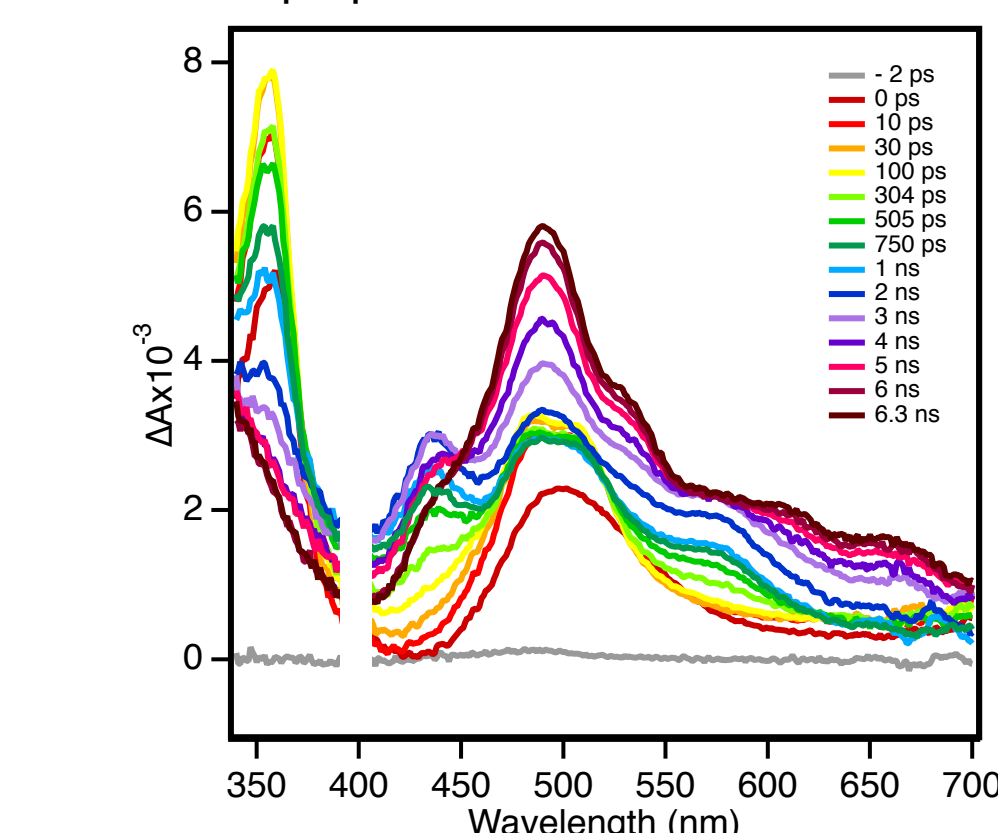


Figure 1. UFTA spectrum of [IrCp*(bpy)H]⁺ in the presence of methanol after 400 nm excitation.

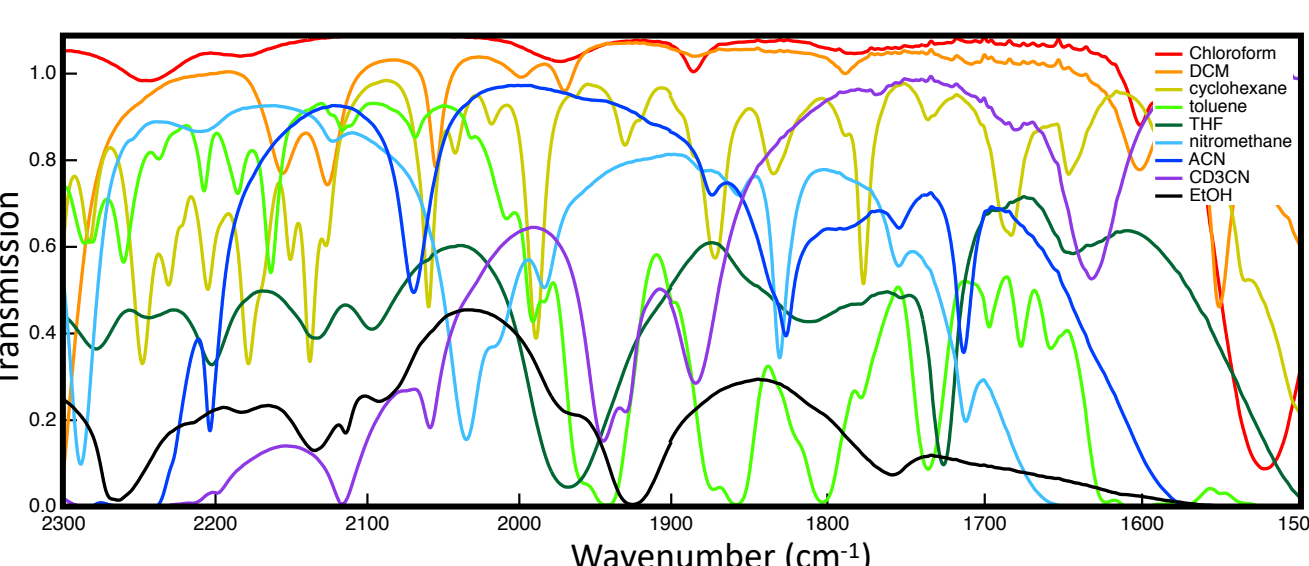


Figure 4. FTIR spectra of a variety of solvents.

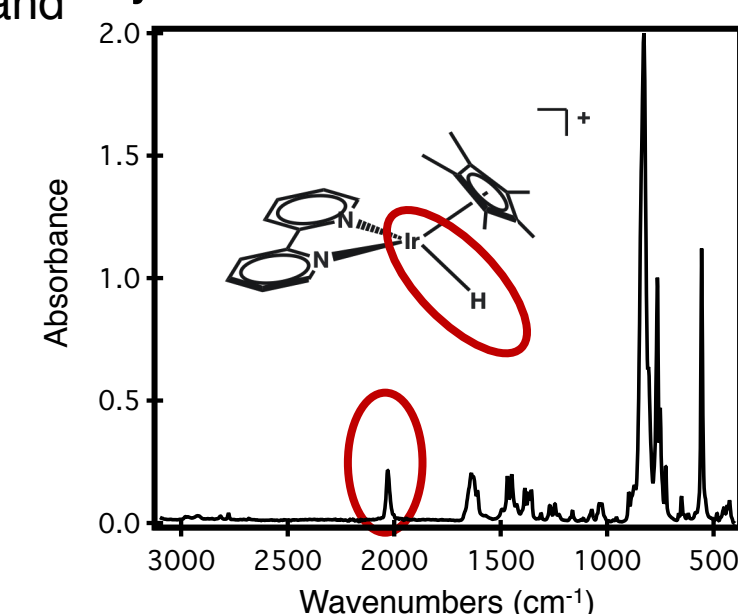


Figure 2. Experimental solid-state ATR-FTIR spectrum of [IrCp*(bpy)H]⁺. Red highlight indicates Ir-H stretching mode.

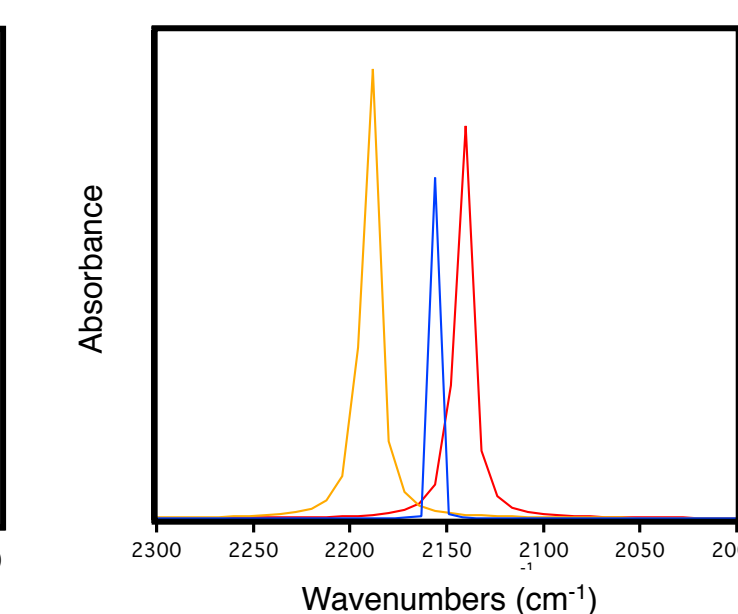


Figure 3. DFT-calculated stretching modes of complexes highlighted in Scheme 1.

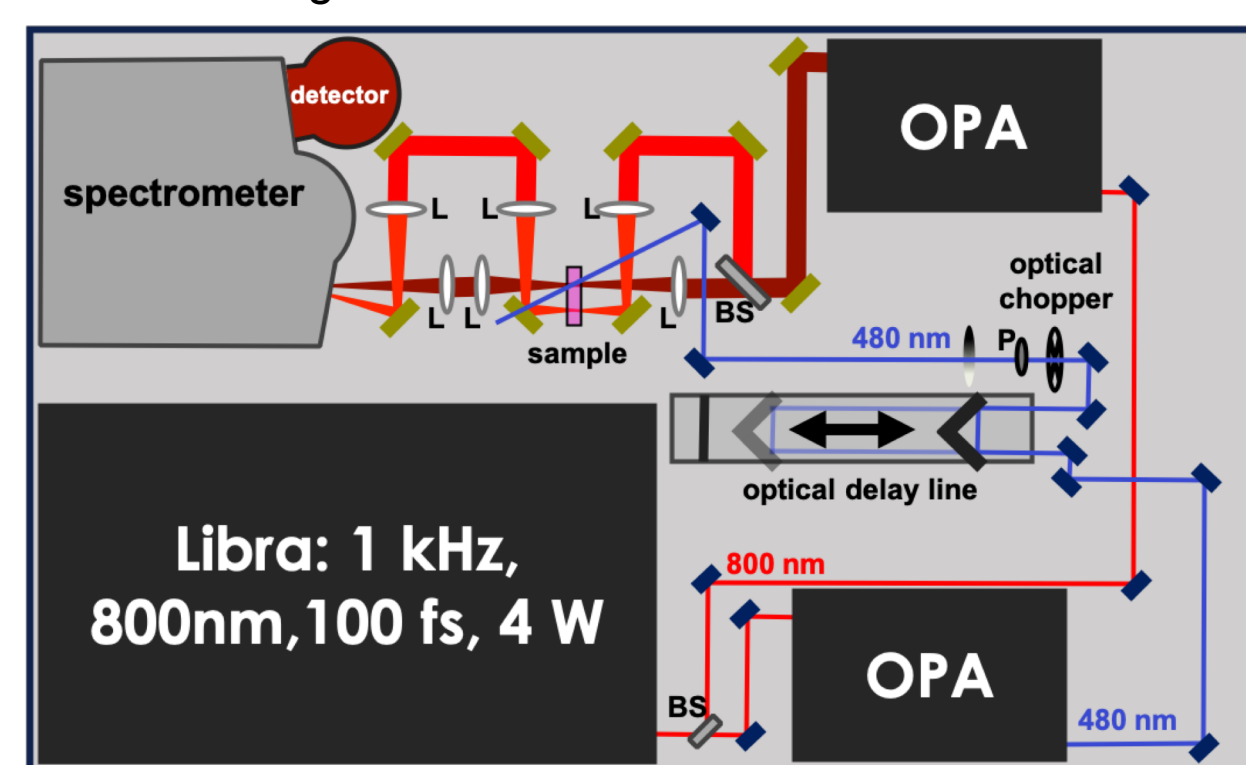
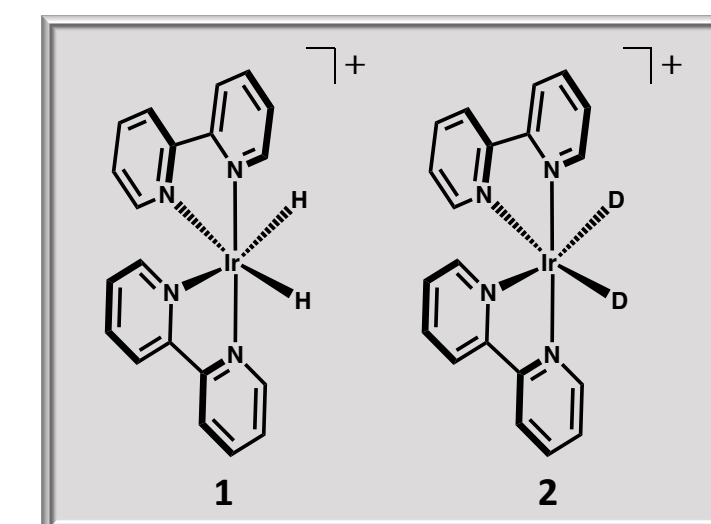


Figure 5. Schematic of our ultrafast TRIR setup.

(1) *J. Am. Chem. Soc.* **2016**, *138*, 13509-13512.

Objective

- Examine the excited states of complexes **1** (Ir-H) and **2** (Ir-D) (right) via sensitive time-resolved techniques.
- Observe M-H stretching modes for the first time using TRIR spectroscopy.



Vibrational Spectroscopy

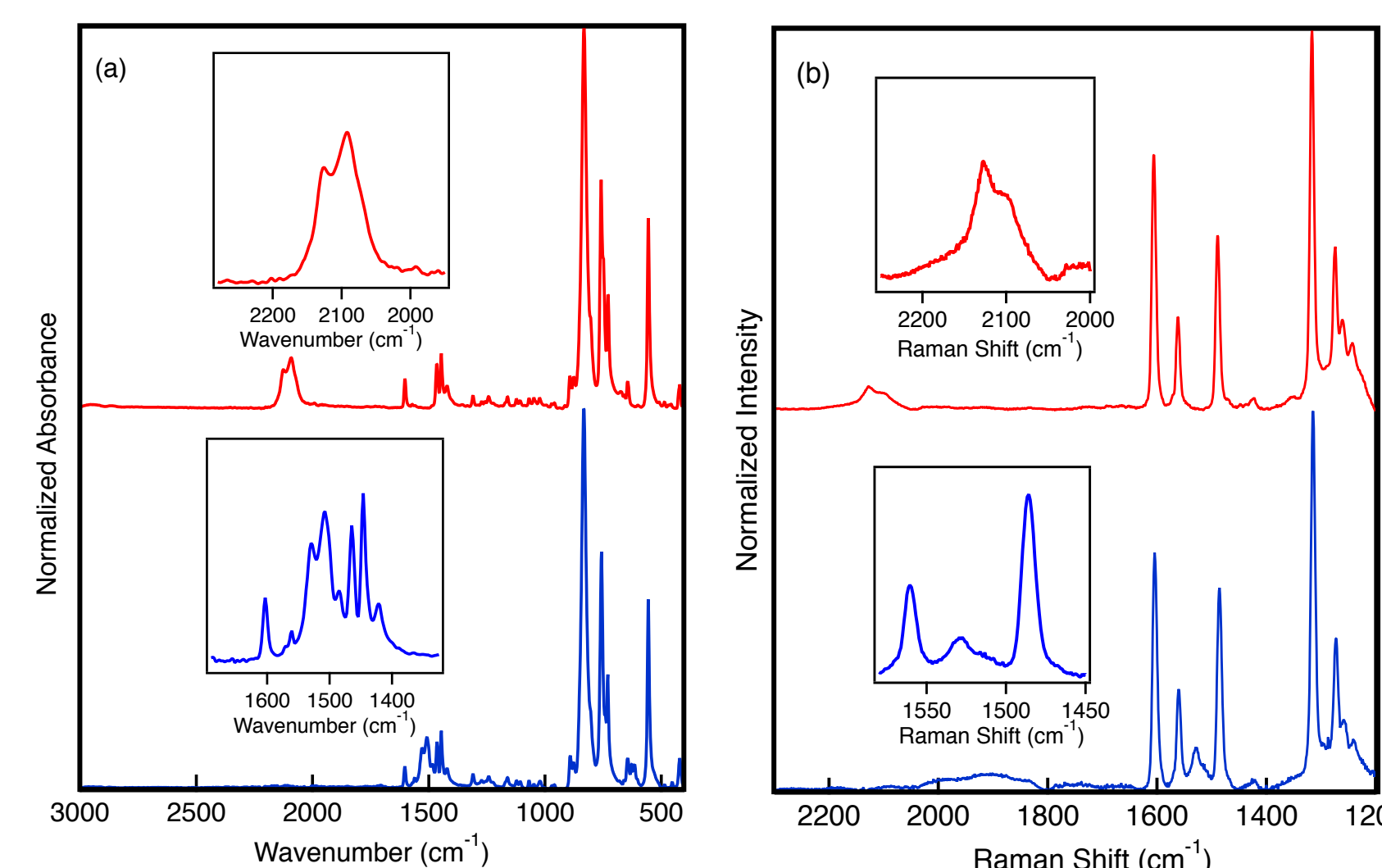
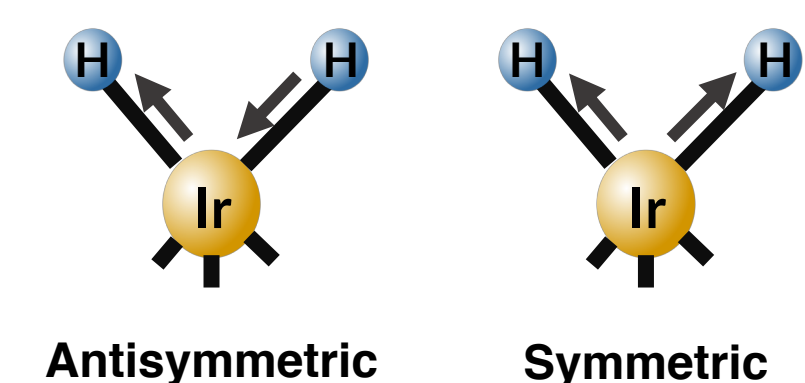


Figure 6. (a) Solid-state FT-IR (ATR) and (b) Raman spectra ($\lambda_{\text{ex}} = 785 \text{ nm}$) of **1** (red) and **2** (blue). Insets depict enlarged Ir-H and Ir-D modes.



Easy to identify Ir-H and Ir-D stretching modes...

$$\mu = \frac{m_a m_b}{m_a + m_b}$$

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Ultrafast Dynamics

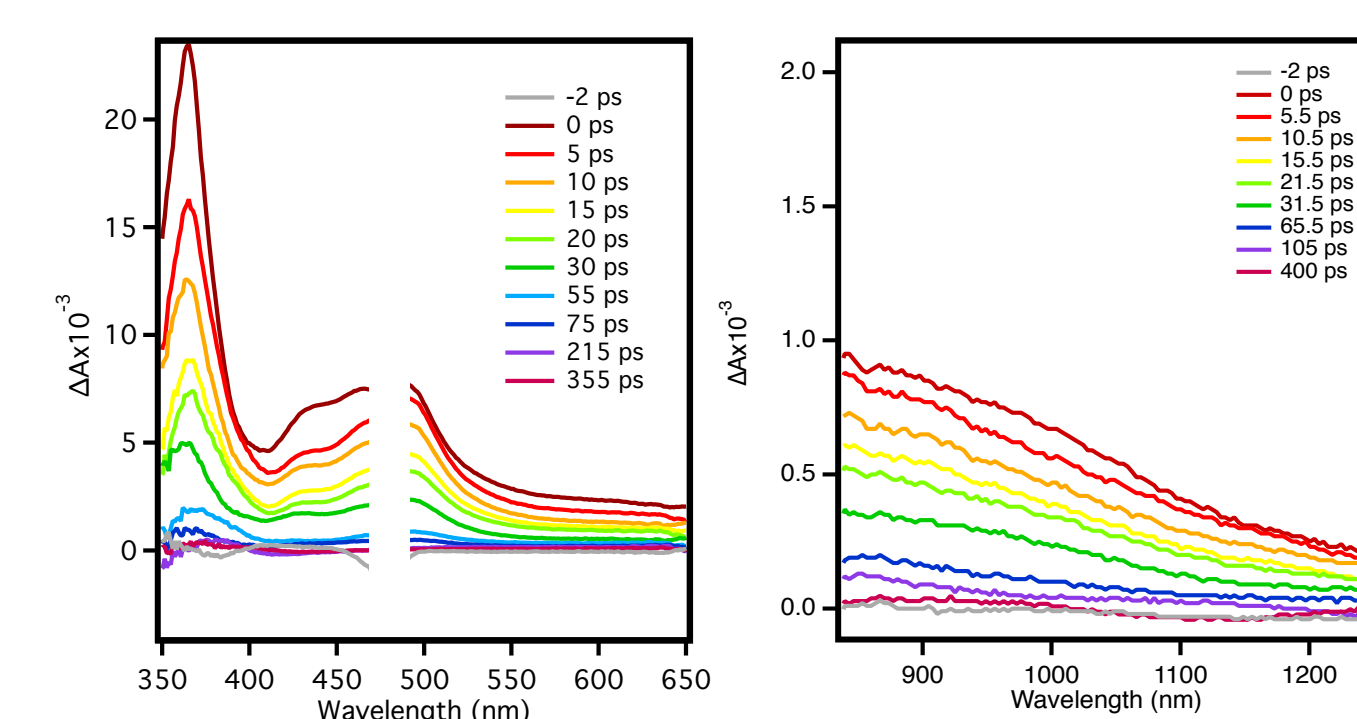


Figure 7. UFTA difference spectra of **1** measured in acetonitrile following excitation by 480 nm laser pulses. NIR difference spectra are also shown on right. Laser scatter at excitation wavelength removed for clarity.

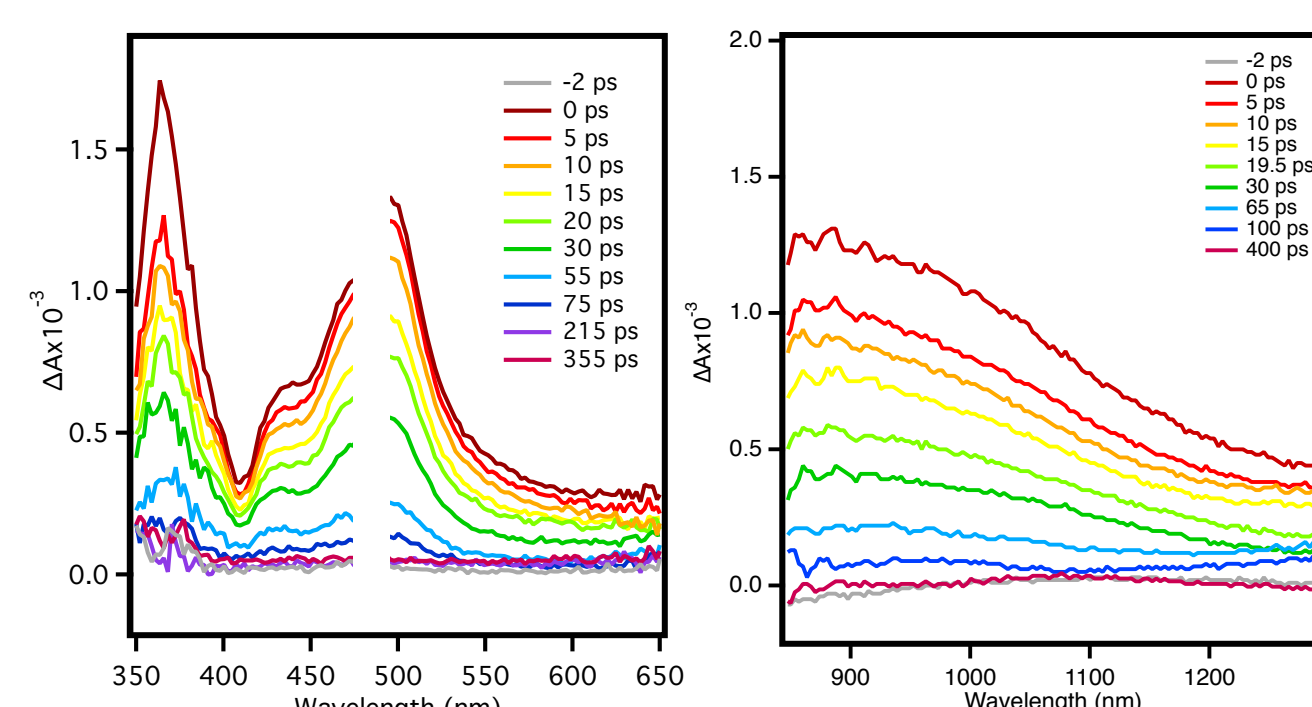


Figure 8. UFTA difference spectra of **2** measured in acetonitrile following excitation by 480 nm laser pulses. NIR difference spectra are also shown on right. Laser scatter at excitation wavelength removed for clarity.

Short-lived excited state! ~25 ps for both complexes.

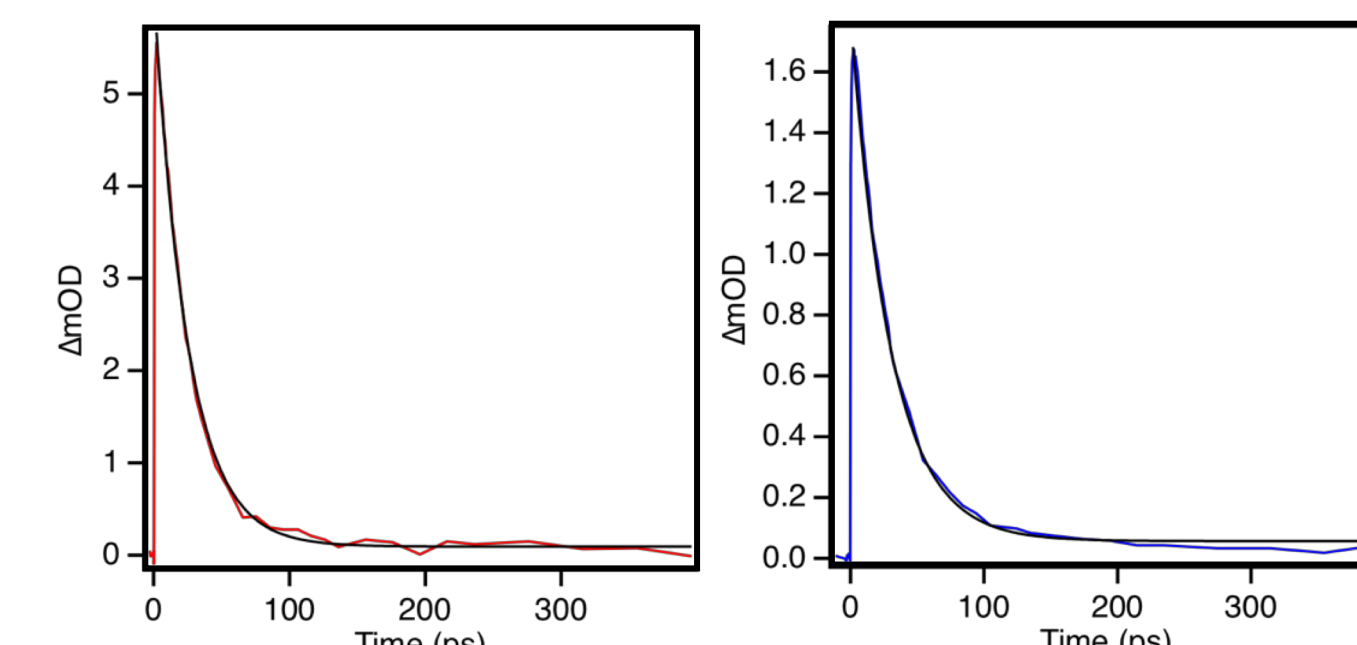
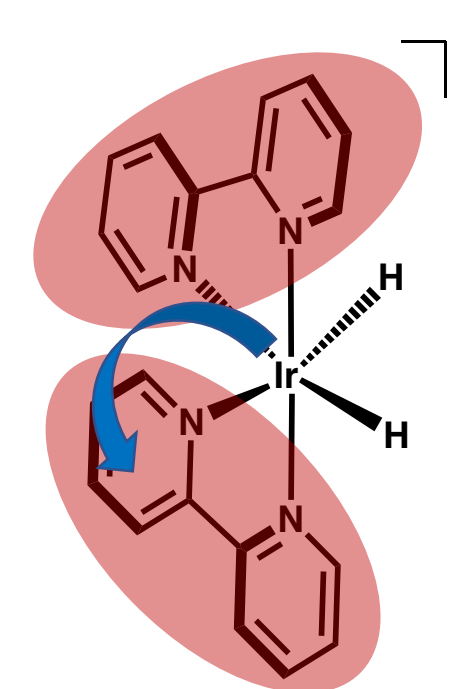


Figure 9. UFTA decay kinetics at 500 nm for **1** (left) and **2** (right).

- UFTA absorbance features match those of the ligand (2,2'-bipyridine) radical anion, confirming metal-to-ligand charge transfer (MLCT) excited state.

- No further spectral evolution observed on longer timescales (nsTA).

- No measurable effect of substituting H for D on lifetime nor absorbance features.



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M-H Stretching Modes Observed with TRIR

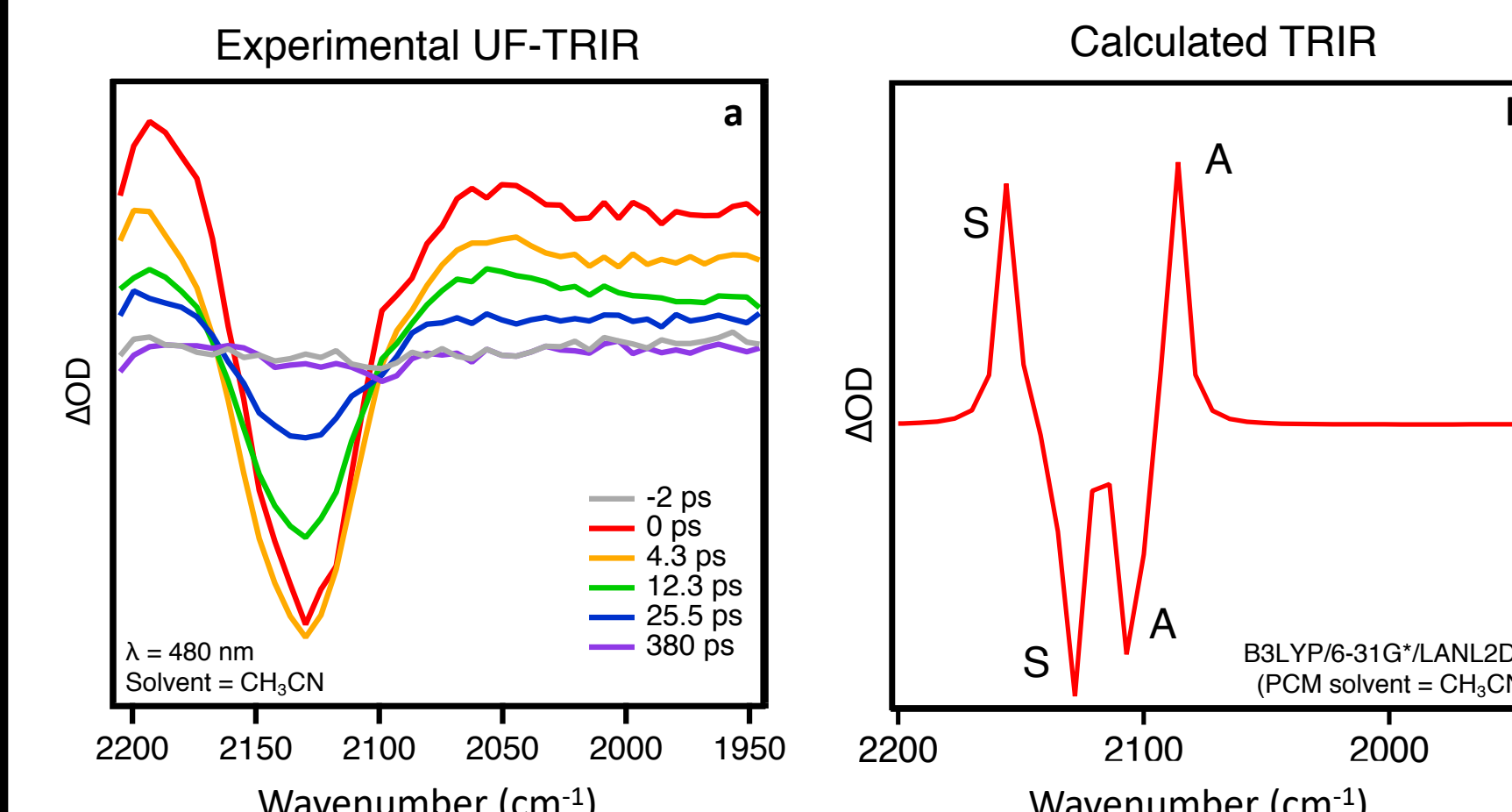


Figure 10. (a) Experimental ultrafast TRIR spectrum of the metal hydride stretching modes of **1** in acetonitrile after 480 nm excitation (b) DFT-simulated TRIR spectrum of **1**.

Ir-H stretching modes successfully observed using TRIR spectroscopy

- Negative feature matches expected frequency of ground state bleach.
- Two positive features assigned as belonging to symmetric (S) and antisymmetric (A) stretches of Ir-H modes after MLCT excitation via DFT calculations.
- No signal observed when monitoring complex **2** at this window.

Observing Ir-D Modes with TRIR?

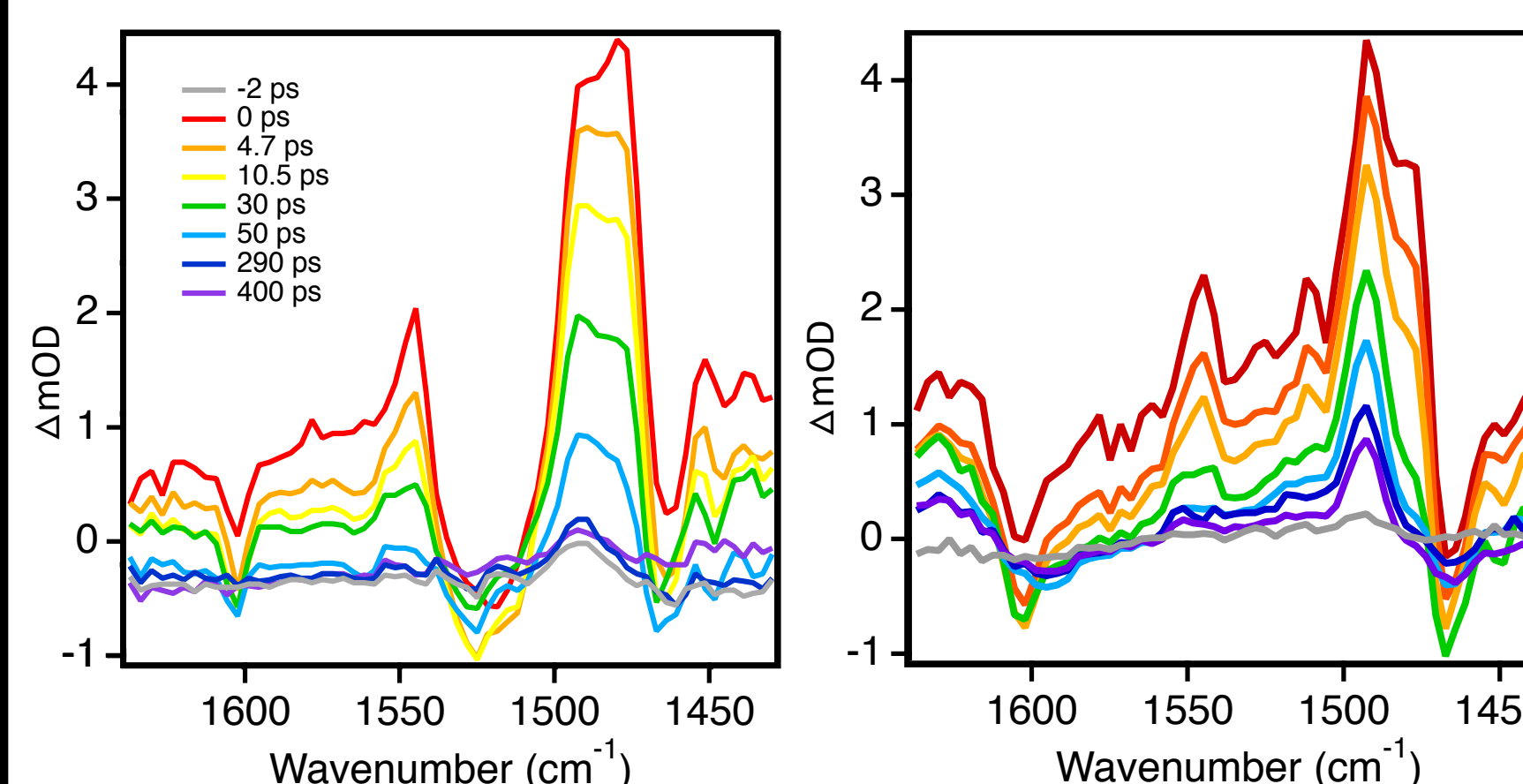


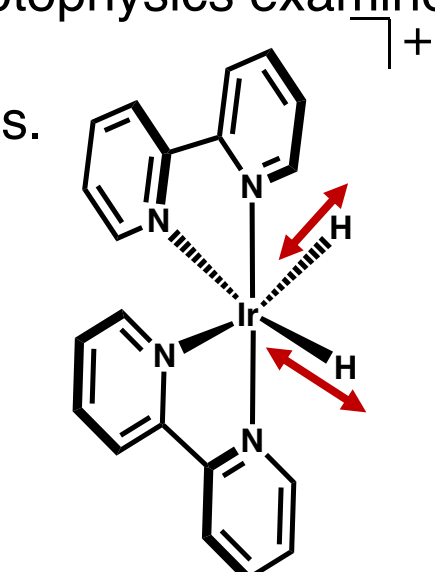
Figure 11. Ultrafast TRIR spectrum of **2** (left) and **1** (right) at the lower energy window centered at the Ir-D bleach in the presence of deuterated acetonitrile after 480 nm excitation.

Ir-D stretches masked by ligand breathing modes

- Prominent ground state bleach belonging to Ir-D stretching modes in **2** is surrounded by many positive features.
- Difficult to assign positive features as the Ir-D vibrations lie in between ligand breathing modes.
- Upon replicating experiment with **1** at this window, the positive features are still present, suggesting they belong to ligand modes.

Conclusions

- Complexes *cis*-[Ir(bpy)₂H₂]⁺ (**1**) and *cis*-[Ir(bpy)₂D₂]⁺ (**2**) were synthesized and their photophysics examined.
- Static vibrational spectra revealed weak but measurable Ir-H and Ir-D stretching modes.
- TA measurements reveal a short-lived MLCT excited state ($\tau = 25 \text{ ps}$).
- Ir-H stretching modes successfully observed using ultrafast TRIR
- Ir-D stretching modes masked by ligand-localized modes.
- Results presented here are a stepping stone for future photophysical measurements (particularly utilizing TRIR) on more photoactive Ir(III) hydrides.



Acknowledgments

