# 超快时间分辨 X 射线吸收谱光催化过程瞬态结构表征

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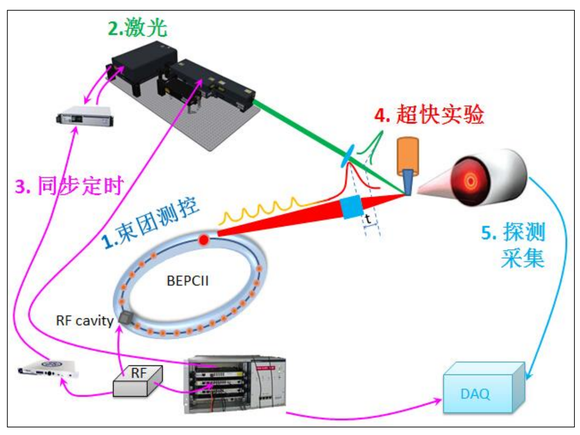
## 简介

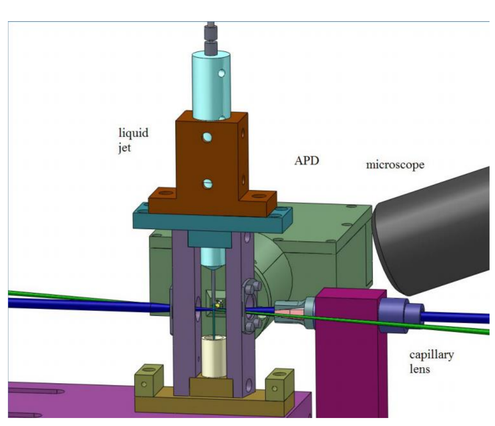
时间分辨激光泵浦-X射线探测技术提供一种独特的方法研究化学、生物、材料科学中的动力学过程，从原子分子尺度研究这些非平衡态过程的几何结构和电子结构演化，给出光催化反应过程的分子电影。

## 时间分辨X射线实验方法

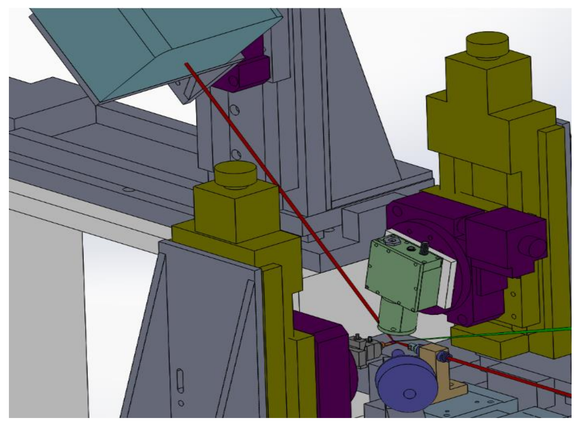
超快时间分辨实验先由一束脉冲激光将样品激发，然后由一束X光在不同延迟进行探测，得到激发后不同驰豫时间的中间物种信息。在BSRF的1W2B线站已经建立超快吸收谱（TR-XAS）和衍射谱（TR-XRD）两种时间分辨技术，时间分辨达到150皮秒。 TR-XAS技术是光催化机理研究量身定裁的实验方法。




实验装置示意

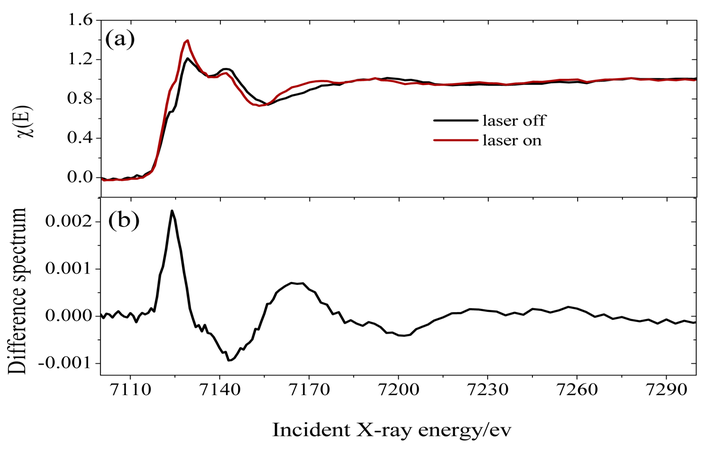


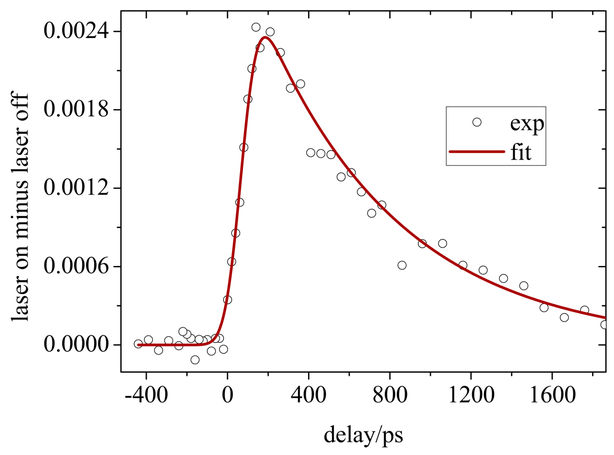

溶液样品TR-XAS

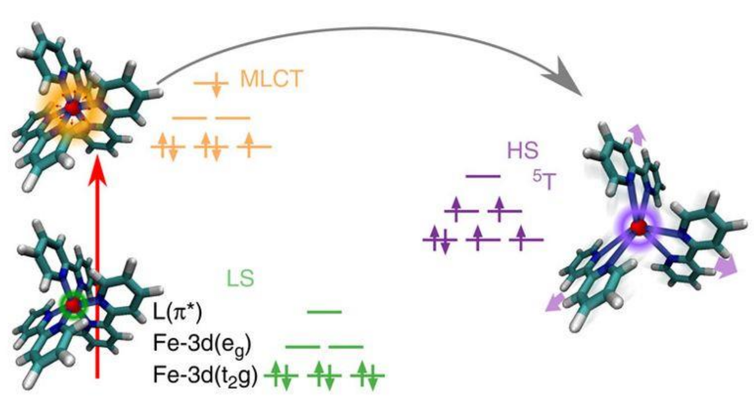


薄膜样品TR-XAS和TR-XRD联测

**Fe化合物自旋翻转：** 亚毫摩尔浓度(0.3mM)$[Fe^{II}(phen)^3]^{2+}$，低自旋基态激发后转变为高自旋激发态

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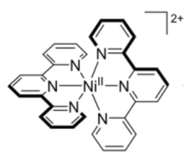
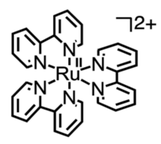
**Ni均相光催化$CO_2$还原：**

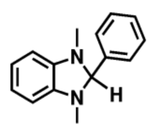
催化剂

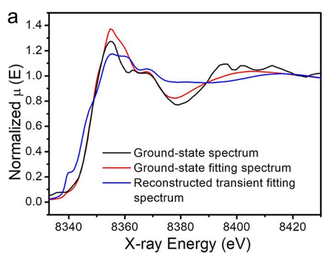


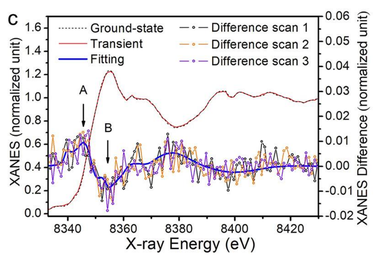
光敏剂

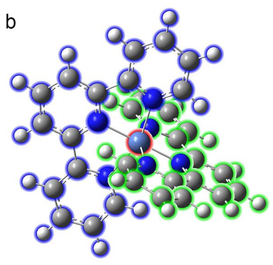


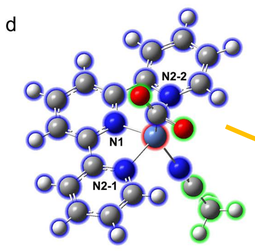
电子牺牲剂

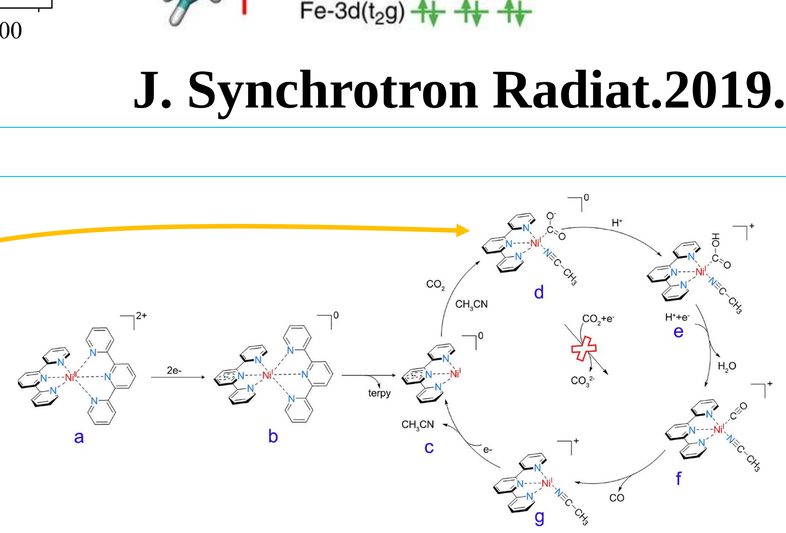




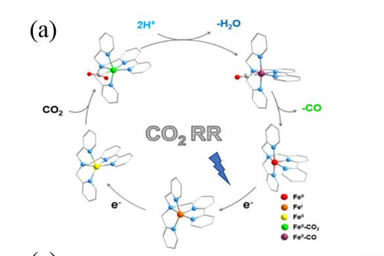



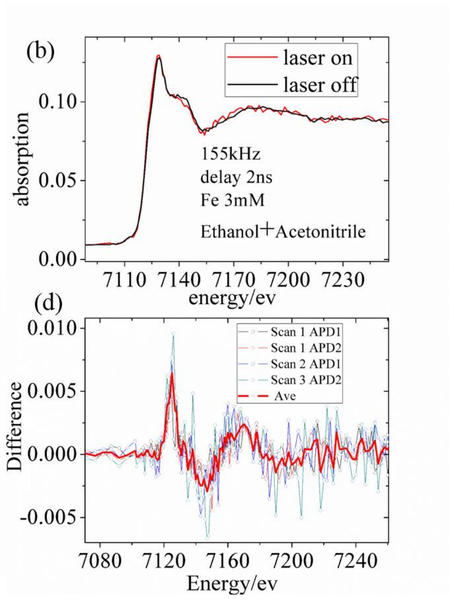




TR-XAS实验结合DFT计算表明催化剂得到光敏剂提供的电子后，脱掉一半配体并吸附一个$CO_2$分子，实现$CO_2$还原为CO的催化过程

**Fe自敏化光催化$CO_2$还原：**

光照下发生配体到金属的电荷转移（LMCT），通过TR-XAS测试了光激发后2ns时的瞬态结构，延迟扫描表明光照后瞬态结构驰豫时间为3.7ns




**致谢：** 感谢超快时间分辨组全体成员，感谢中科大和理化所等光催化合作团队

**参考文献：**
Can Yu. et al. Upgrade of laser pump time-resolved X-ray probes in Beijing synchrotron, *Journal of Synchrotron Radiation*, 2019, 26:2075-2080.
Yangguang Hu. et al. Tracking Mechanistic Pathway of Photocatalytic CO2 Reaction at Ni Sites Using Operando, Time-Resolved Spectroscopy, *Journal of the American Chemical Society*, 2020, 142:5618-5626.
Hao Wang. et al, Development of picosecond time-resolved X-ray absorption spectroscopy by high-repetition-rate laser pump/X-ray probe at Beijing Synchrotron Radiation Facility, *Journal of Synchrotron Radiation*, 2017, 24:667-673.