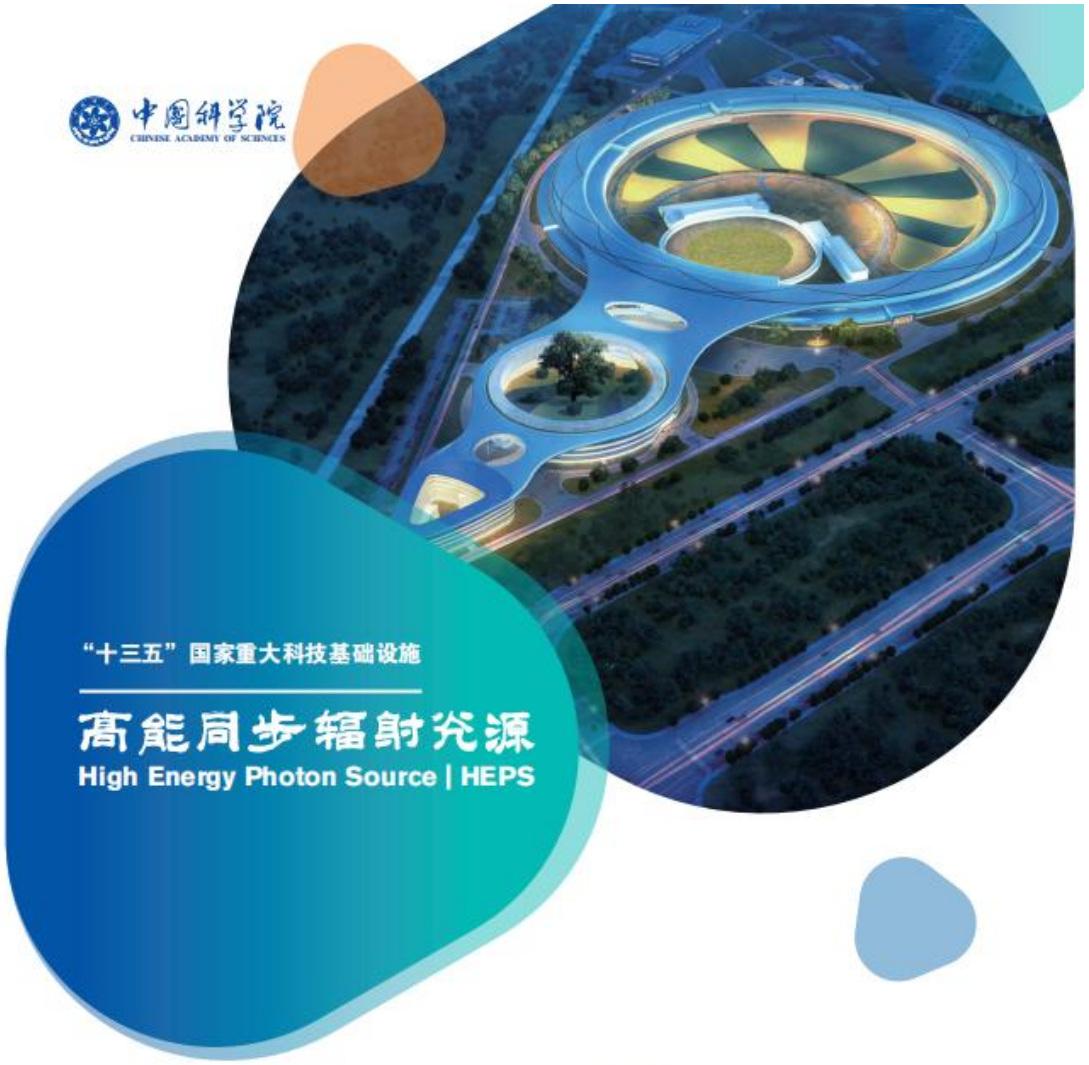
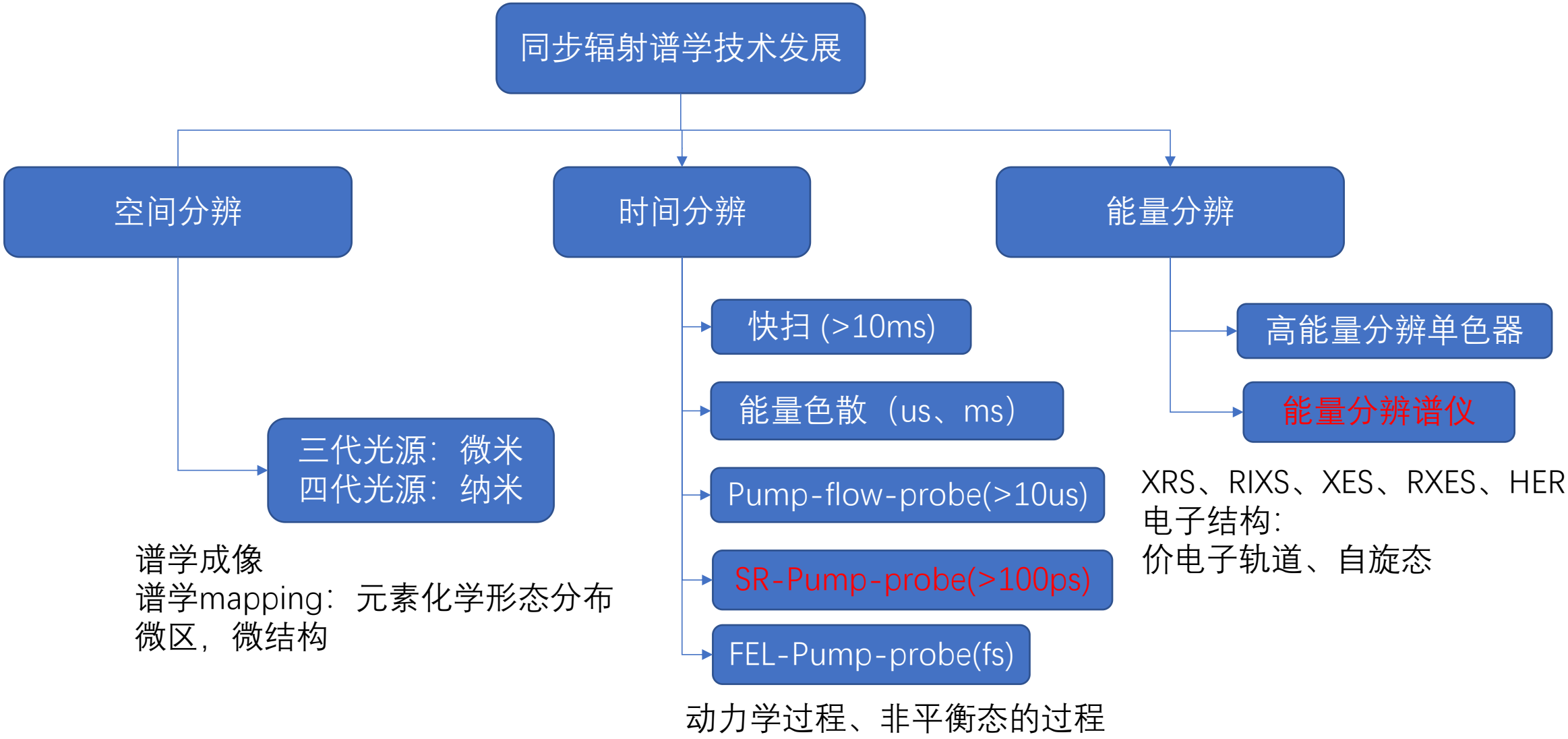


SNS 中国散裂中子源 China Spallation Neutron Source

先进X射线谱学技术发展和应用

报告人：余灿
职位：博后
合作导师：陈洁、郑黎荣
日期：2022.6.30

未来X射线谱学技术发展

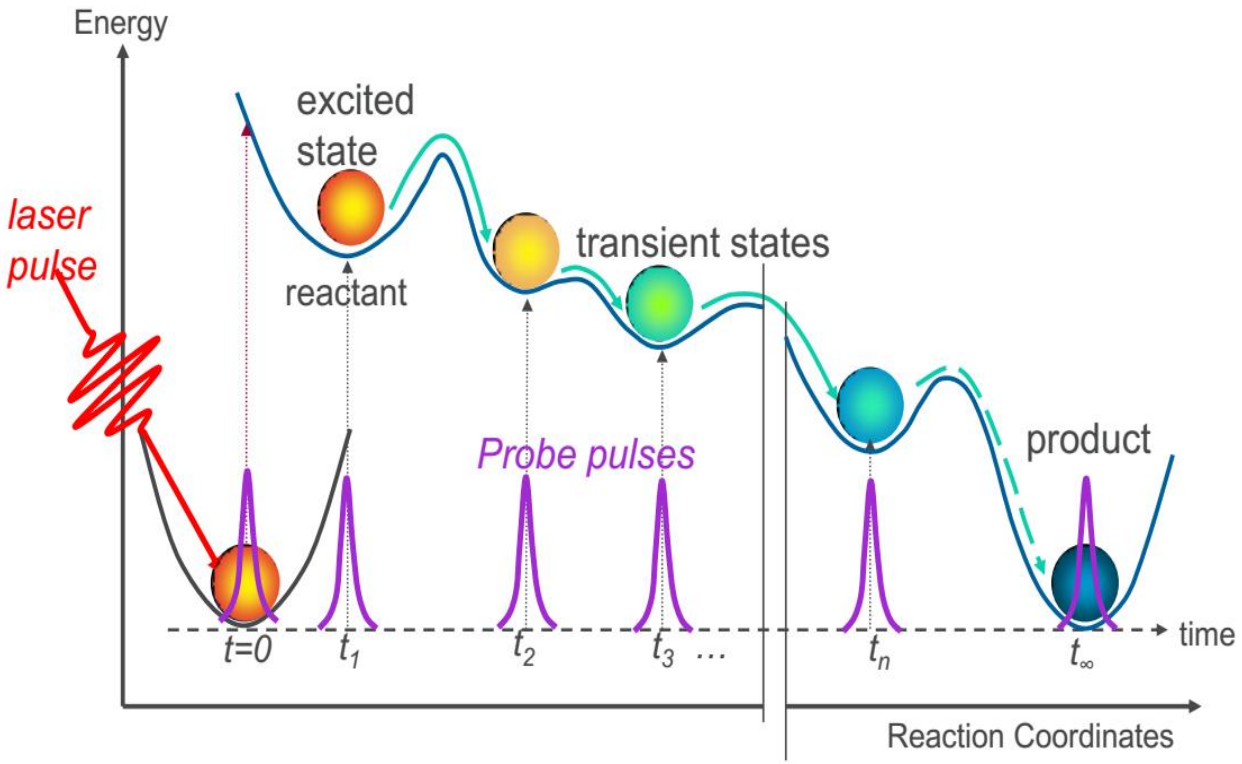


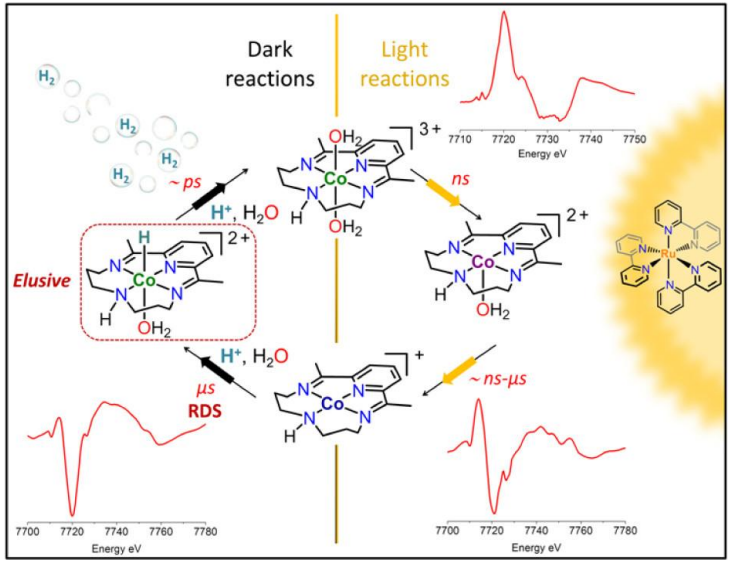
Outline

- Pump-probe超快时间分辨吸收谱发展
  1、Cu-Co光催化体系完整催化反应机理
  2、Fe自敏化催化体系
  3、Ce催化剂光敏裂瞬态过程研究

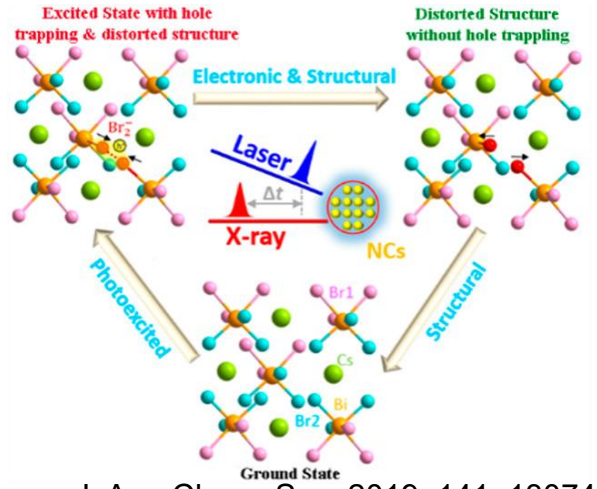
- 高能量分辨吸收谱实验方法发展
  1、高能量分辨谱仪设计和样机研制
  2、HERFD应用

Pump-probe实验方法



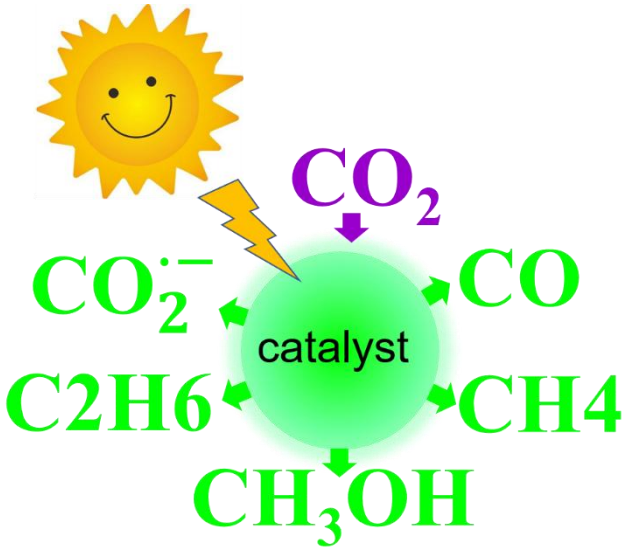


J. Am. Chem. Soc. 2016, 138, 10586−10596

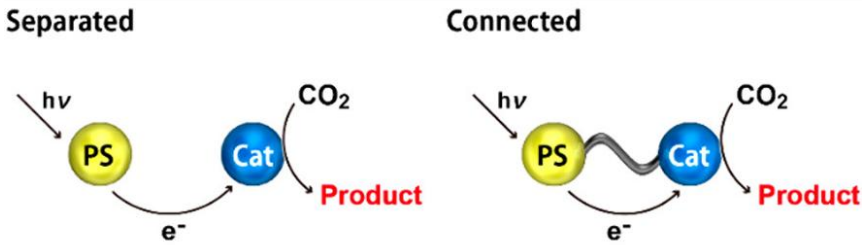


J. Am. Chem. Soc. 2019, 141, 13074−13080

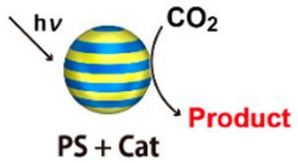
光催化反应机理研究



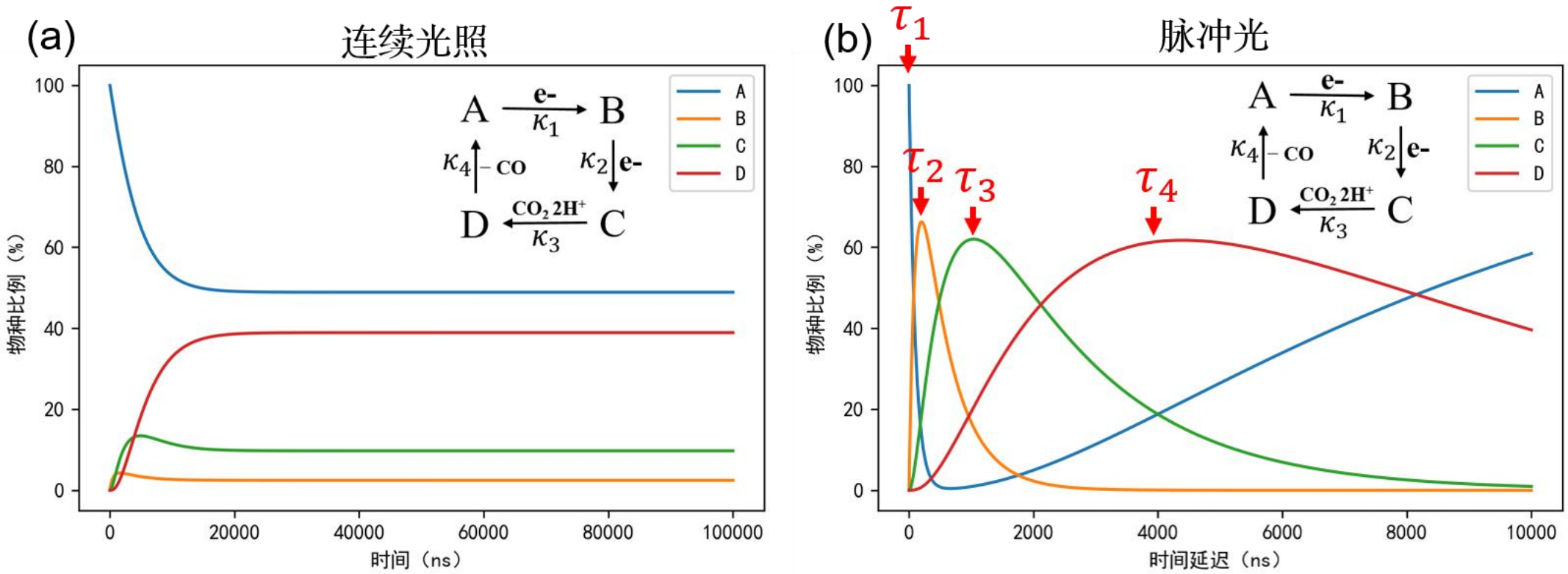
一：功能分离系统



二：自敏化体系

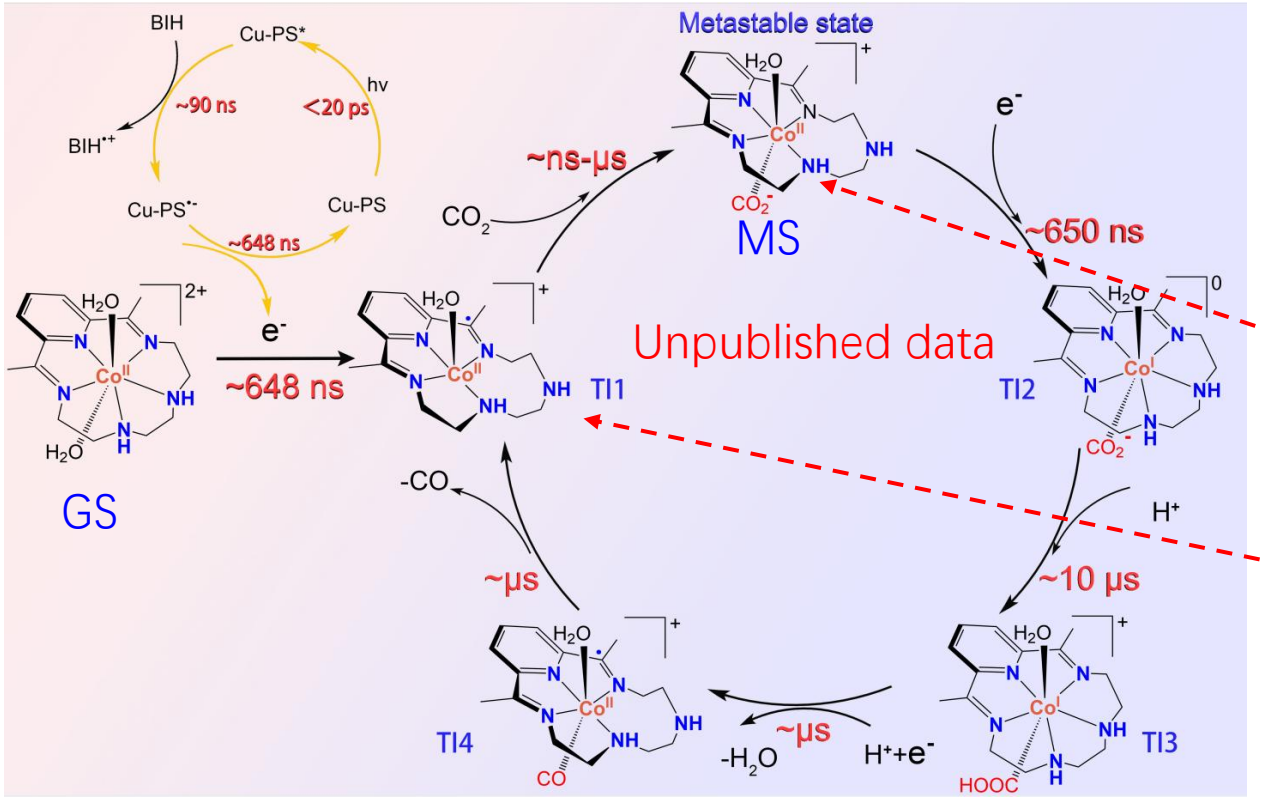


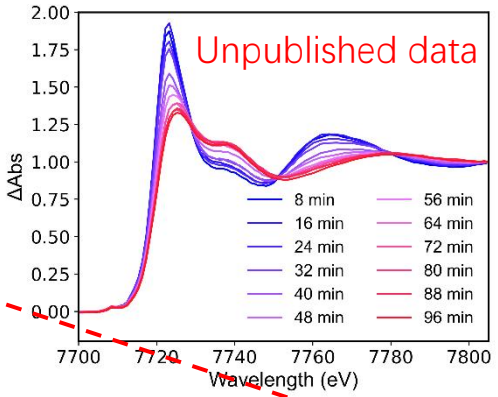
原位光照和pump-probe的瞬态研究



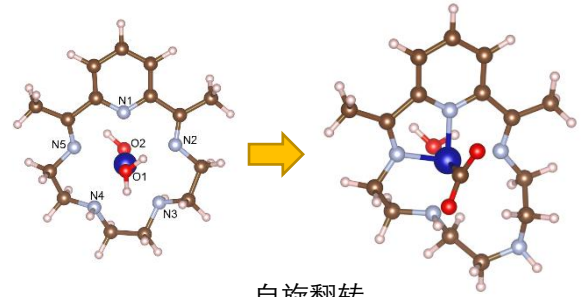
Cu-Co光催化（中科大熊宇杰组）

DFT+XTA：获得完整的催化反应路径

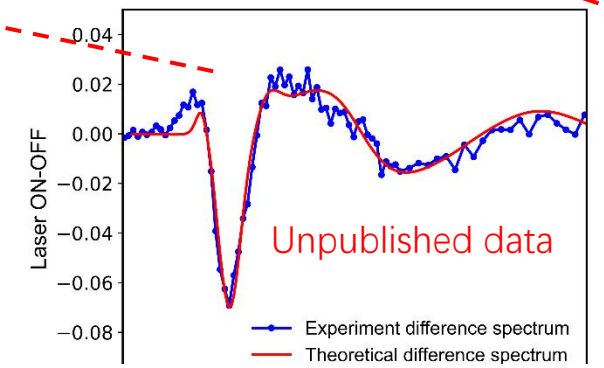


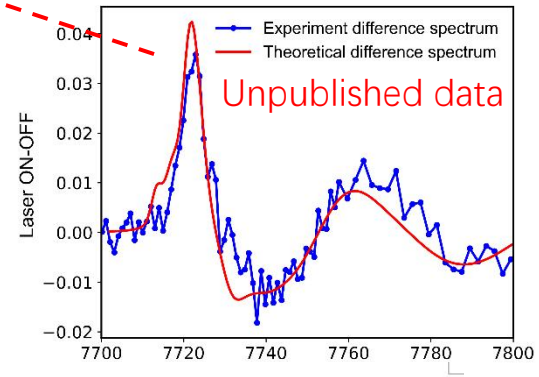


基态到亚稳态的双物种转换



捕获多个关键的反应中间态



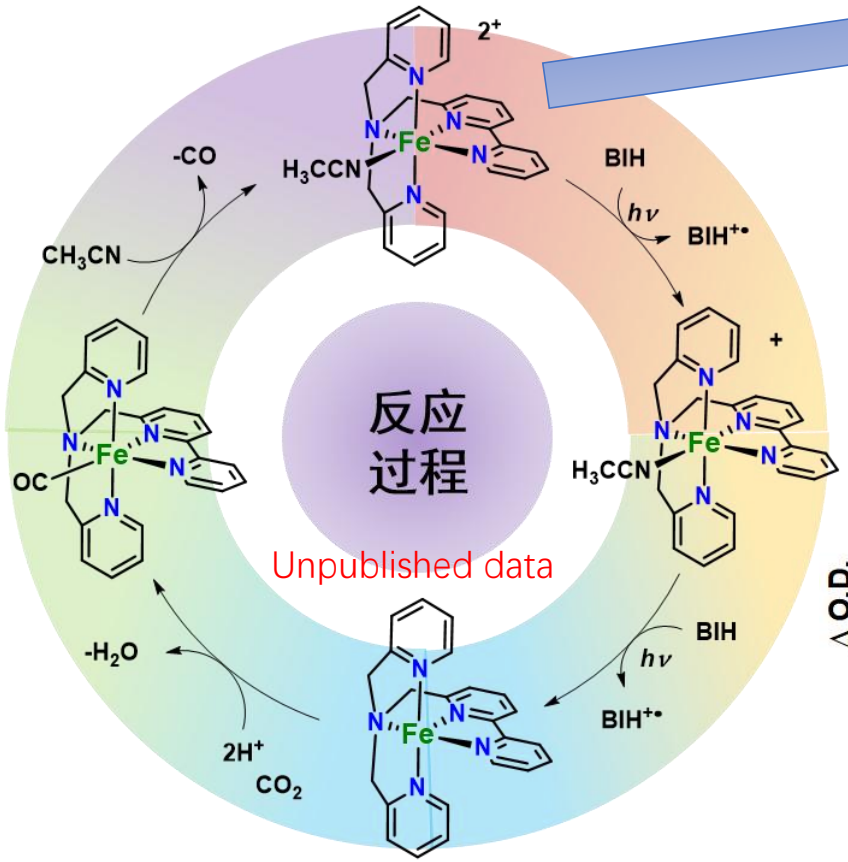


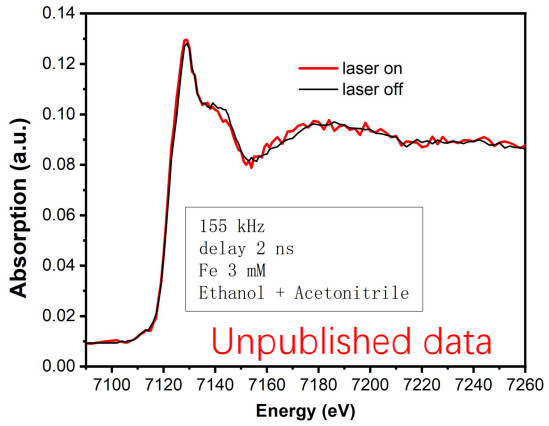
Direct evidence of ligand reorganization for the promotion of high-efficiency reaction in photocatalytic CO_2 reduction

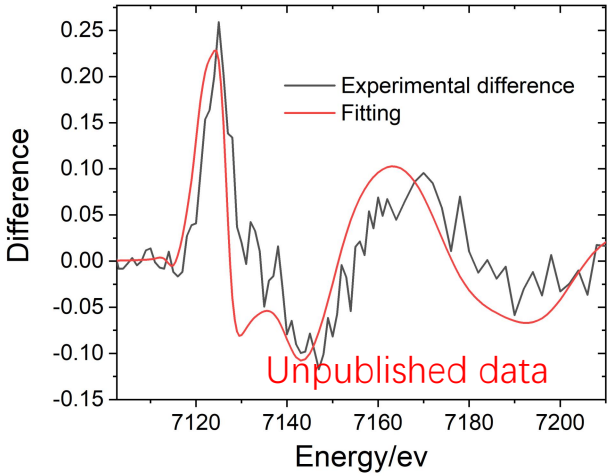
Yangguang Hu[1,†], Can Yu[2,4†], Qian Wang[1,†], Fei Zhan[3], Hao Wang[2,5], Lei Li[1], Guozhen Zhang[1,*], Chao Gao[1,*], Jun Jiang[1], Ye Tao[2,*], and Yujie Xiong[1,*][1]Hefei National Laboratory for

Fe自敏化催化体系（理化所 吴骊珠组）

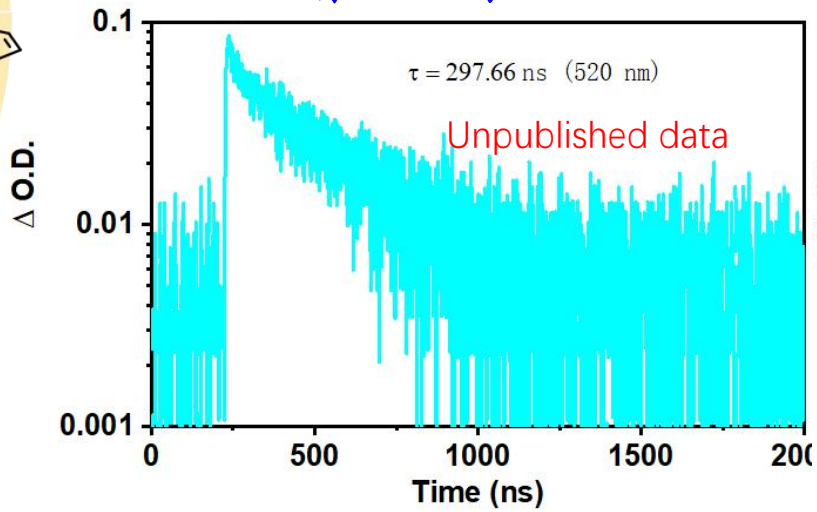
无需光敏剂



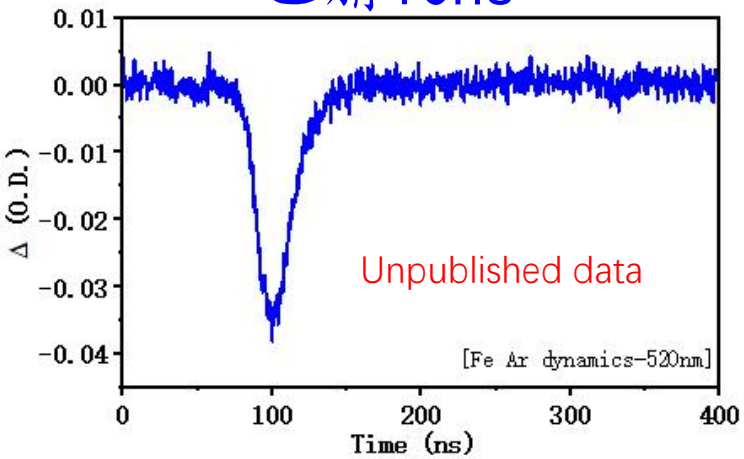




乙腈+乙醇 300ns



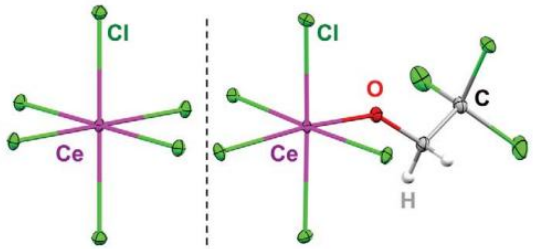
乙腈10ns



已经获得X射线自由激光和国外时间分辨同步辐射机时进一步研究

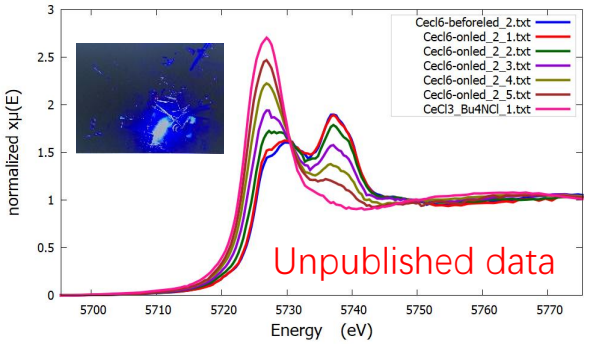
光催化 C–H 活化(武汉大学 雷爱文组)

甲氧基还是Cl自由基的皲裂？？？



$[NEt_4]_2[CeCl_6]$ (1)　　$[NEt_4]_2[CeCl_5(OCH_2CCl_3)]$ (2)

TR-XAS：皲裂物种的捕获



原位结果

烷烃活化

ORGANIC CHEMISTRY

Selective functionalization of methane, ethane, and higher alkanes by cerium photocatalysis

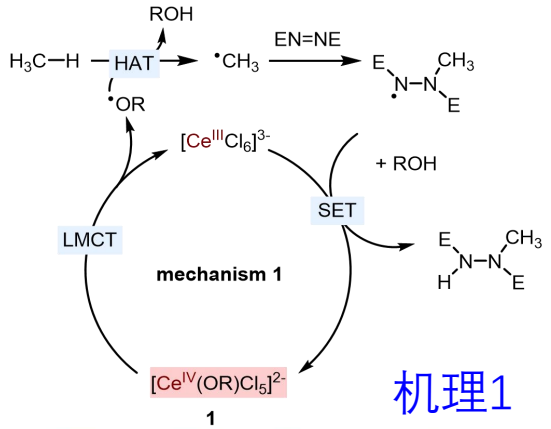
Anhua Hu*, Jing-Jing Guo*, Hui Pan, Zhiwei Zuo†

ORGANIC CHEMISTRY

Photocatalytic C–H activation and the subtle role of chlorine radical complexation in reactivity

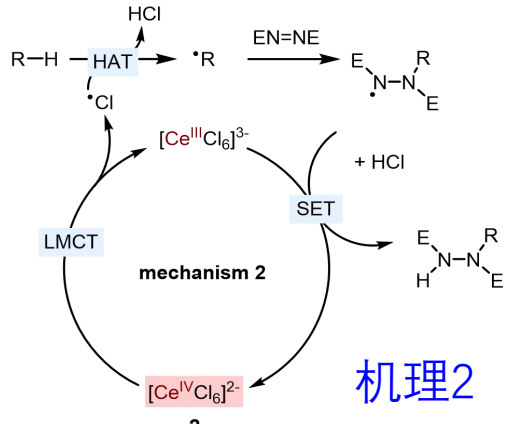
Qiaomu Yang, Yu-Heng Wang, Yusen Qiao, Michael Gau, Patrick J. Carroll, Patrick J. Walsh*, Eric J. Schelter*

两种机理的争议



机理1

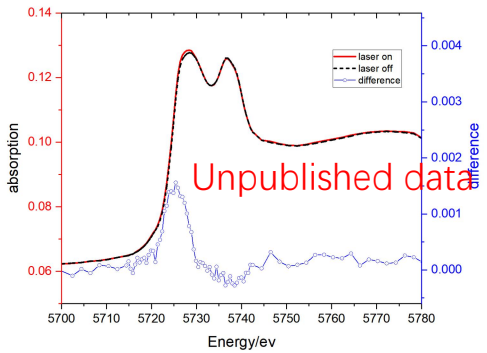
Hu *et al.*, *Science* **361**, 668–672 (2018)



机理2

Yang *et al.*, *Science* **372**, 847–852 (2021)

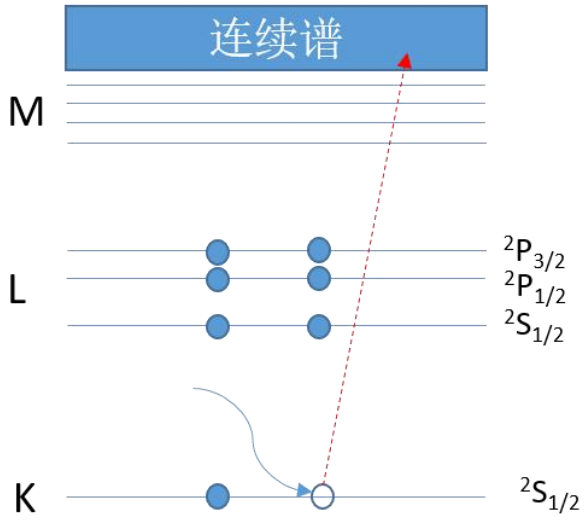
TR-XAS结果

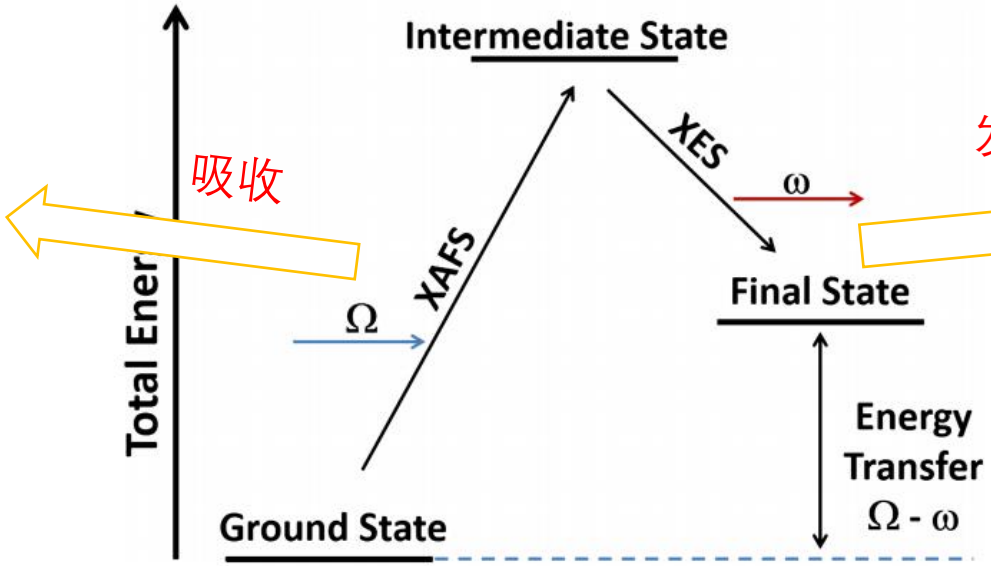


利用原位XAS和瞬态吸收谱结果，来解决Ce催化剂两种催化机理的争议问题，目前的实验结果比较支持机理1。

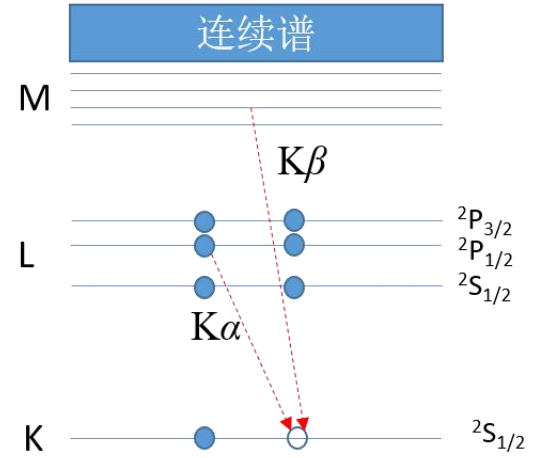
X射线吸收和发射

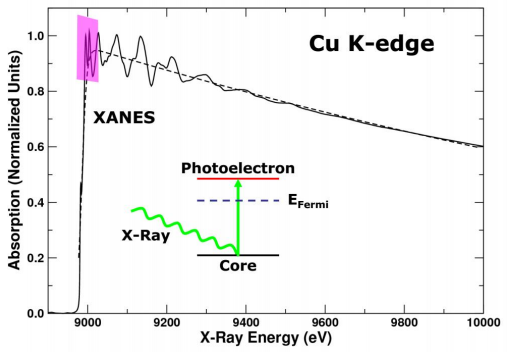
分析晶体谱仪





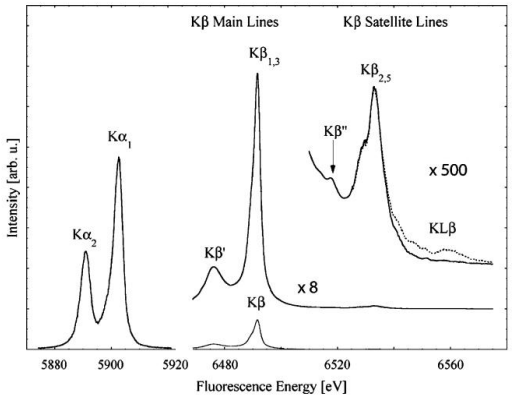
发射





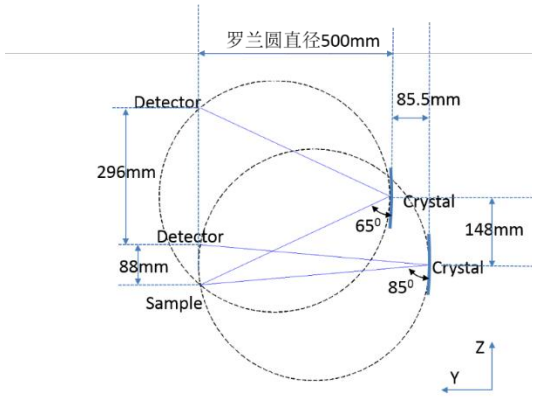
X射线光入光出过程

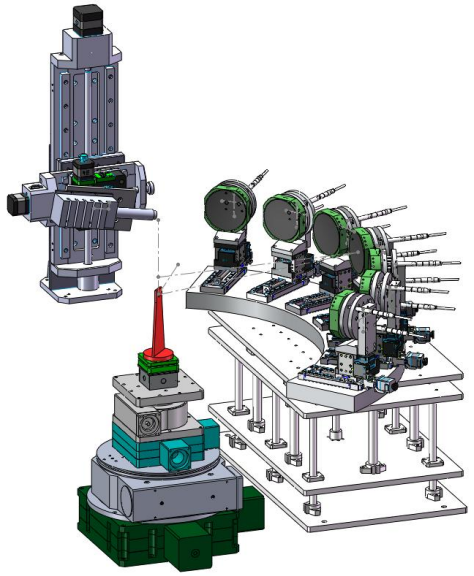
XAS：扫描入射光能量
XES：扫描发射光能量
HERFD：固定发射能量扫描吸收能量
RIXS：同时扫描吸收能量和发射能量
XRS：扫描能量转移



高能量分辨分析晶体谱仪

方案1

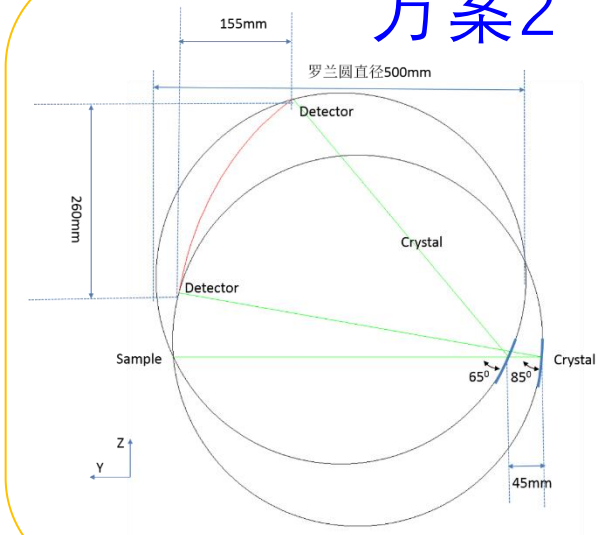


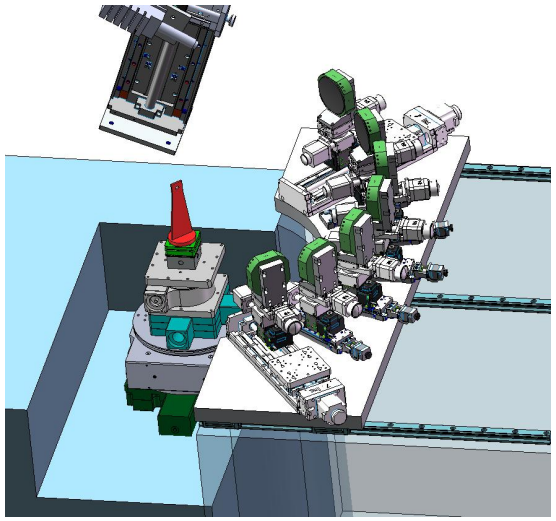


优点：分析晶体可以排列为二维阵列

缺点：调节机构成本高
比较笨重，谱仪需要大范围升降
氦气或者真空腔体不好加

方案2



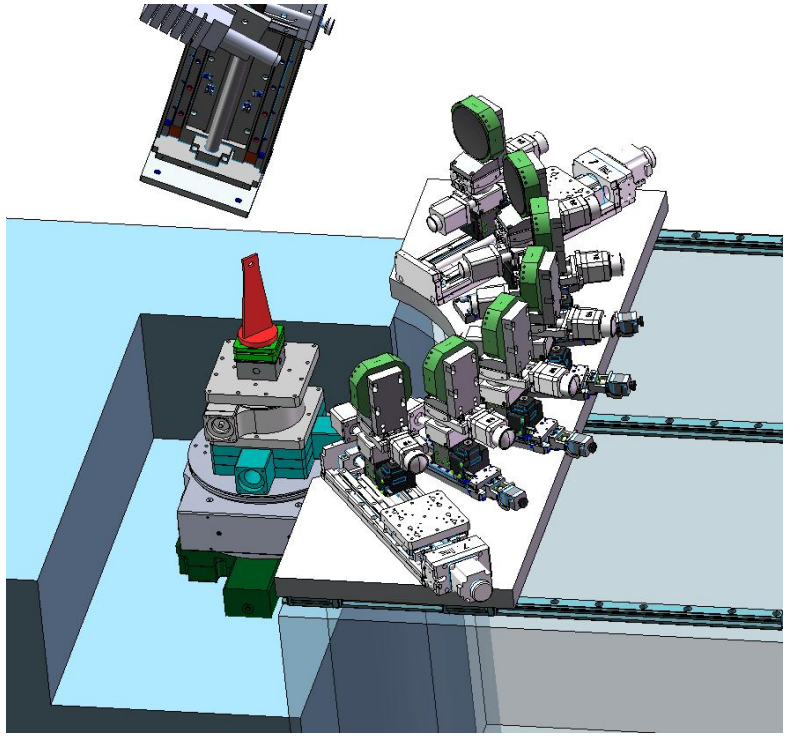


优点：机械设计简化
成本低
方便设计为可变半径罗兰圆
样品处空间更大，方便原位实验

缺点：谱仪调节更为复杂

高能量分辨分析晶体样机

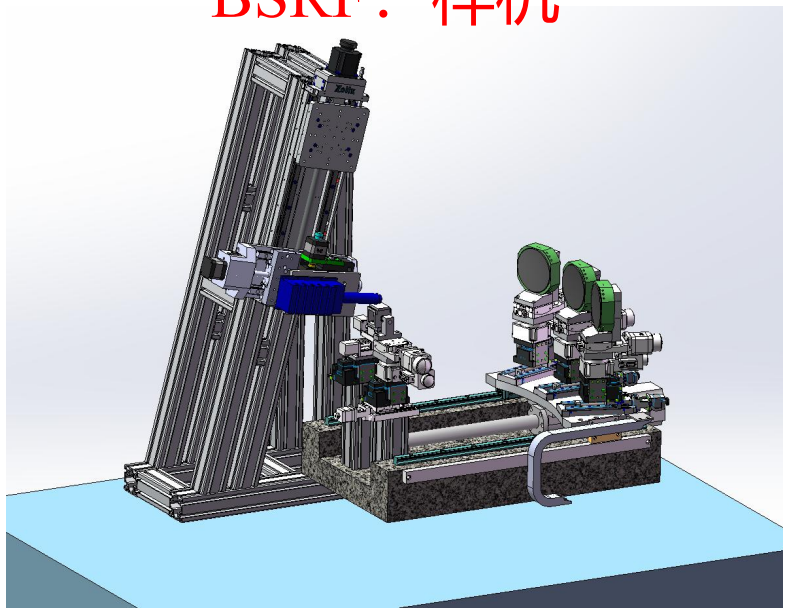
HEPS B8 高七元高分辨谱仪



设计

验证

BSRF：样机



样机目标：

1、验证HEPS七元的机械设计方案，根据样机调试结果优化改进七元方案；

2、谱仪调节优化方案，最终实现自动优化；

3、HERFD、XES、RIXS等实验方法发展；

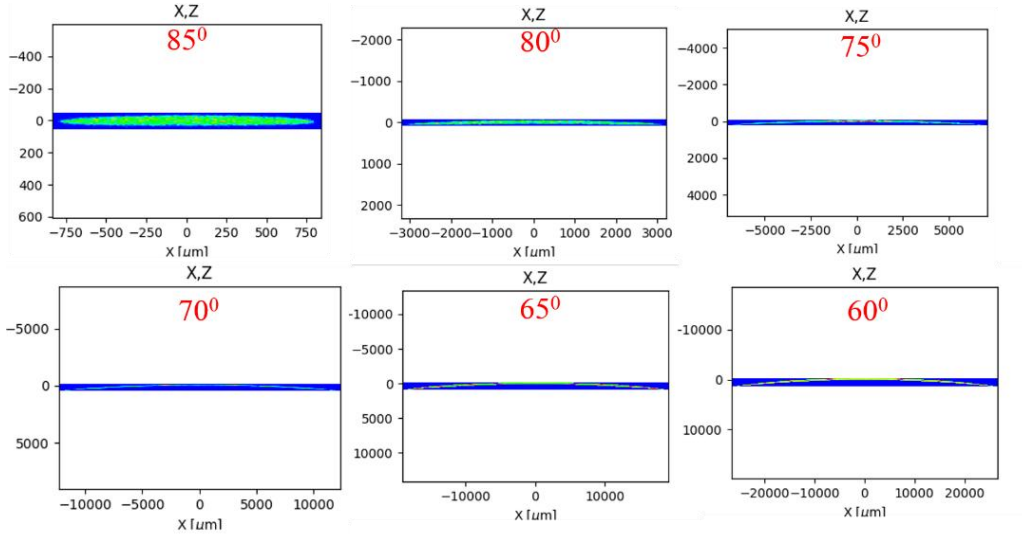
4、提前发展用户群体；目前：北化工、理化所、武大、北京大学

谱仪追迹模拟

表 3 Si(555) 分析晶体在不同布拉格角度下 shadow 模拟结果

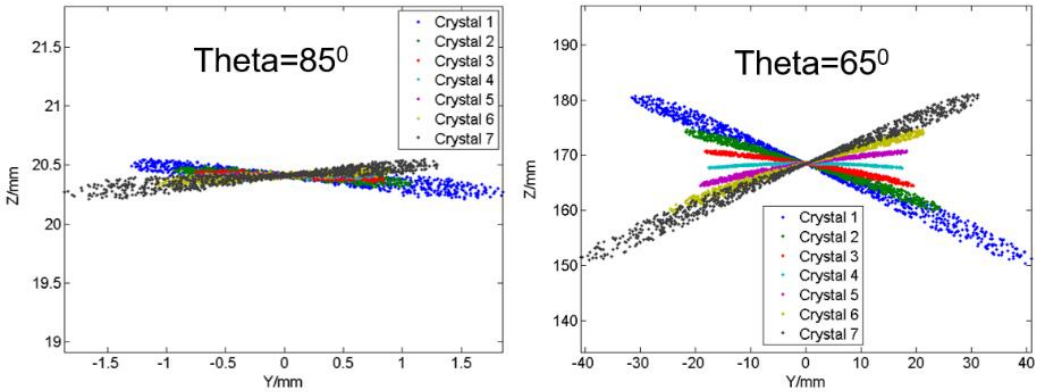
角度	能量/ev	水平光斑大小/mm	能量分辨/ev
85^0	9923.5	1.32	0.5
80^0	10038	5.07	0.98
75^0	10234.5	11.04	1.14
70^0	10520	21.210	2.2
65^0	10907.8	34.9	3.6
60^0	11415	46.4	5.5

能量分辨模拟计算



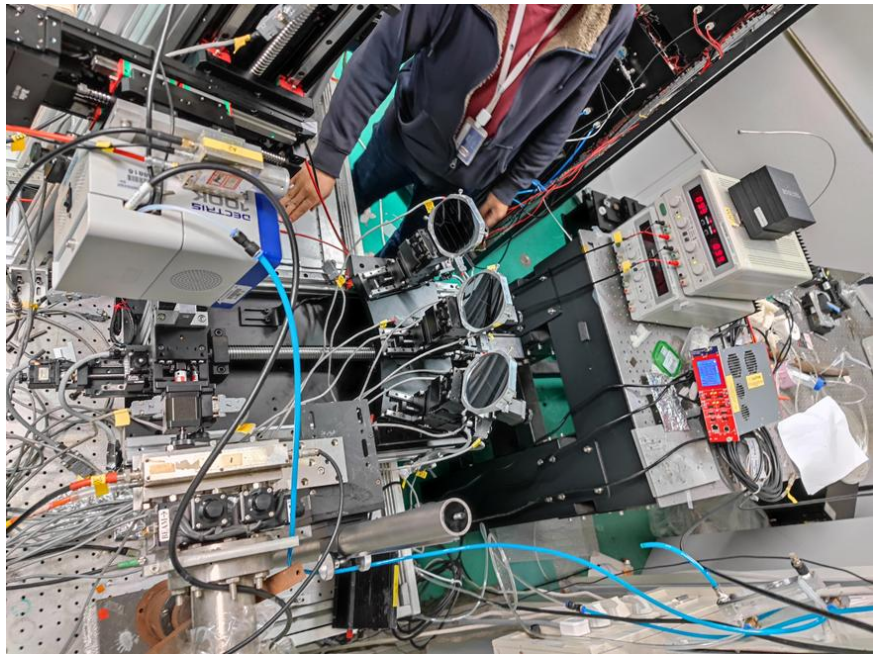
光斑尺寸模拟计算

自己编写的Matlab追迹程序：基于蒙特卡罗算法，也协助于徐伟老师RIXS谱仪追迹

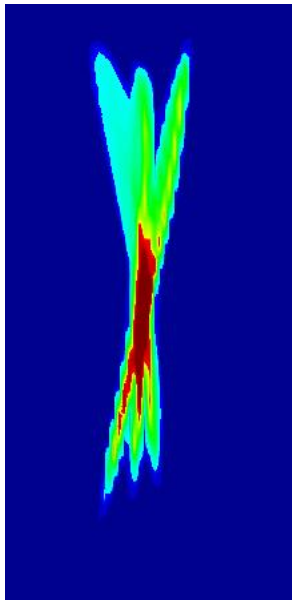


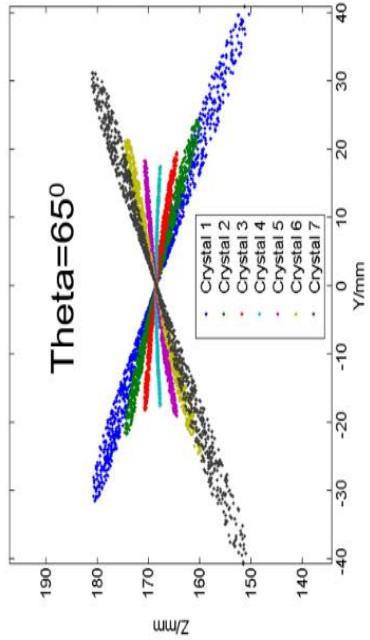
探测器光斑形状追迹

三元样机测试

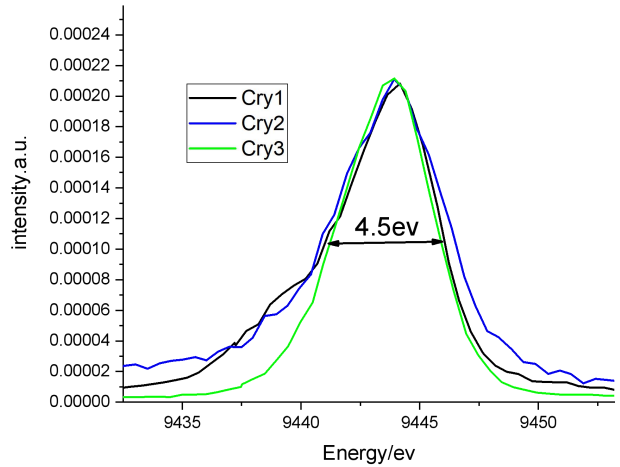


1W2B在线调试



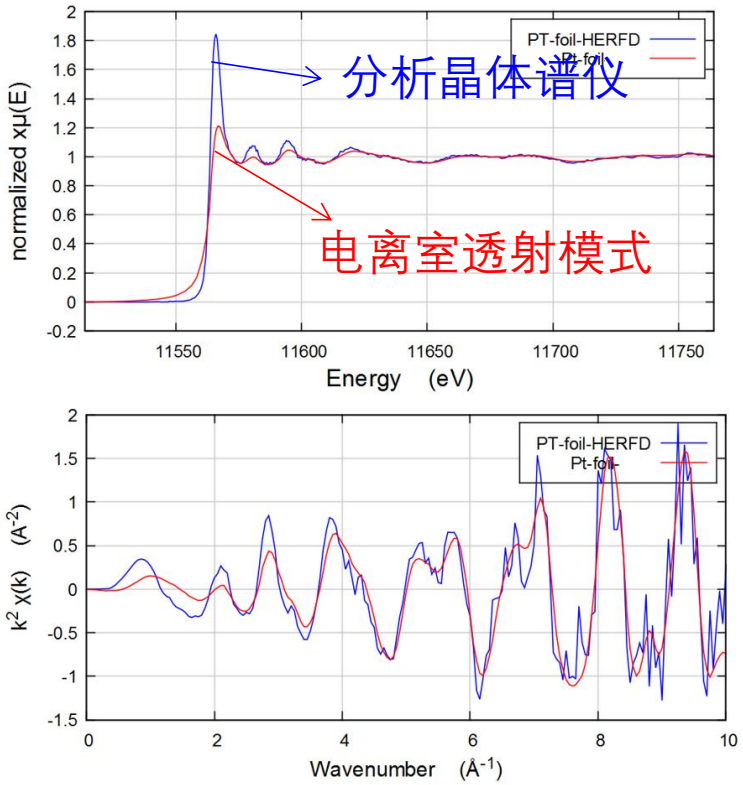


调试结果和模拟一致

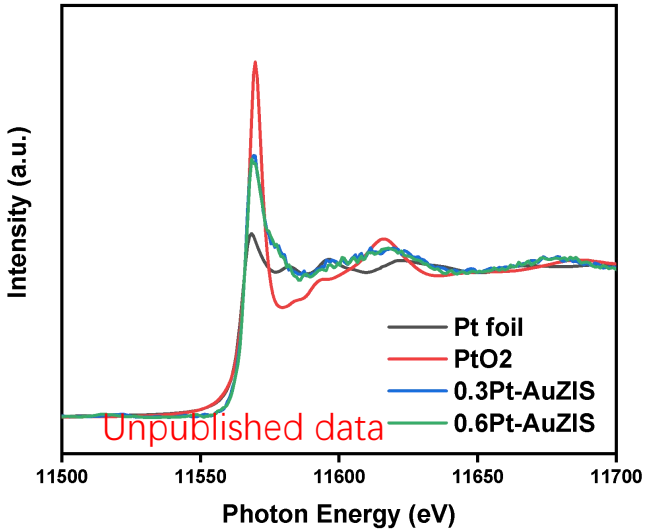


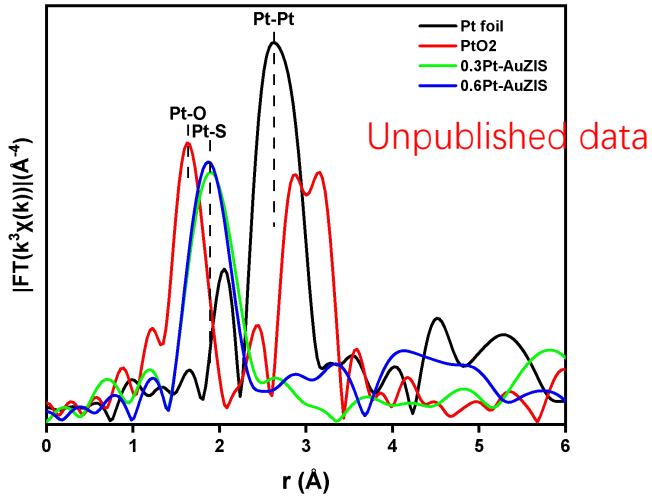
能量分辨扫描结果
解卷积可得到2ev左右能量分辨

分析晶体谱仪应用



清华单原子样品测试结果
消除Zn的本底干扰





高能量分辨吸收谱：锐化进边特征

谢谢大家
请各位老师指导