

# TES x-ray detectors for high efficiency spectroscopy of hemoglobin and other proteins



C.J. Titus<sup>1</sup>, M.L. Baker<sup>1</sup>, H.-M. Cho<sup>2</sup>, W.B. Doriese<sup>3</sup>, J.W. Fowler<sup>3</sup>, G.C. Hilton<sup>3</sup>, K.D. Irwin<sup>1,2</sup>, Y.I. Joe<sup>3</sup>, J. Knight<sup>2</sup>, S.J. Lee<sup>2</sup>, D. Li<sup>2</sup>, R. Marks<sup>2</sup>, K.M. Morgan<sup>3</sup>, D. Nordlund<sup>2</sup>, G.C. O'Neil<sup>3</sup>, C.D. Reintsema<sup>3</sup>, D.R. Schmidt<sup>3</sup>, E. Solomon<sup>1</sup>, D. Sorakas<sup>2</sup>, D.S. Swetz<sup>3</sup>, J.N. Ullom<sup>3</sup>, T.C. Weng<sup>2</sup>, C. Williams<sup>1</sup>, B.A. Young<sup>1,4</sup>  
<sup>1</sup>Stanford University, Stanford, USA, <sup>2</sup>National Institute of Standards and Technology, Boulder, USA, <sup>3</sup>SLAC, Stanford, USA, <sup>4</sup>Santa Clara University, Santa Clara, USA



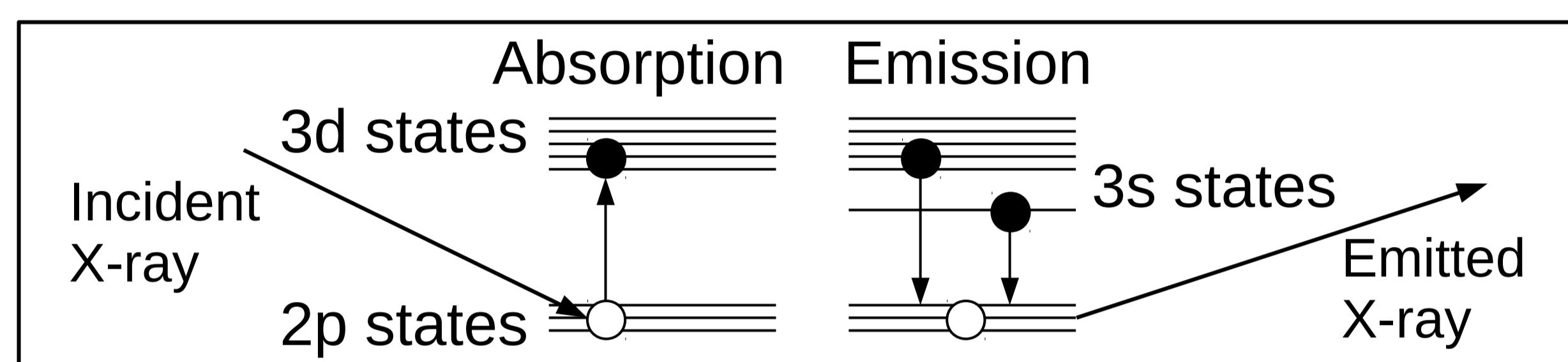
NATIONAL ACCELERATOR LABORATORY

## Solving Molecular Mysteries

Chemists understand reaction mechanisms by probing the properties of the valence (bonding) electrons

- Spin
  - Local Symmetry
  - Oxidation State
- ➔
- More efficient reactions
  - New chemical processes
  - Bio-inspired catalysts

X-ray spectroscopy can probe local electronic structure



Opportunities in proteins

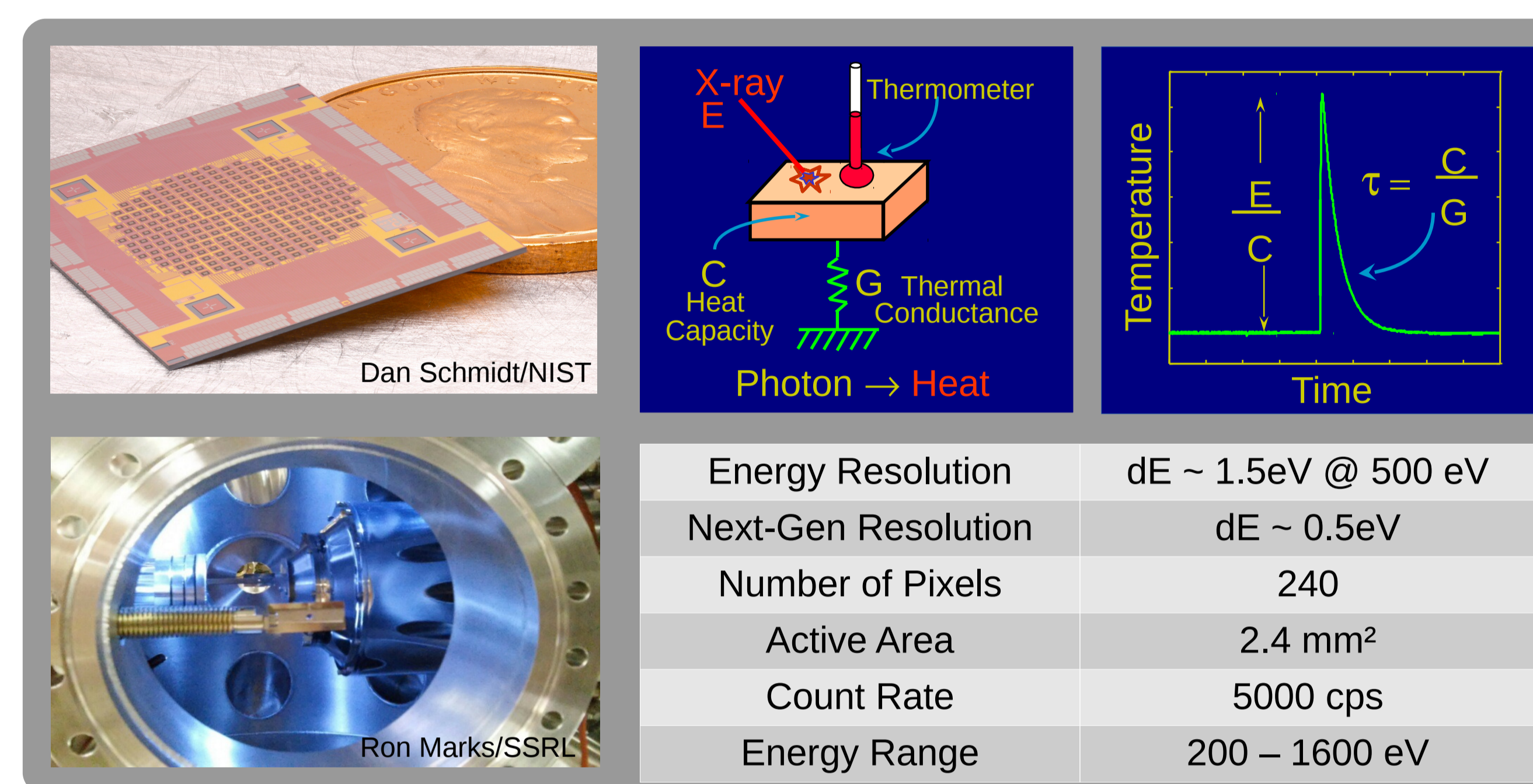
- Probe low concentrations relevant to proteins (< 20 mM)
- Energy-resolved measurements eliminate background
- Proteins hard to probe with other tools (like UV-vis)

## Probing deeper

Transition-edge sensors expand spectroscopy

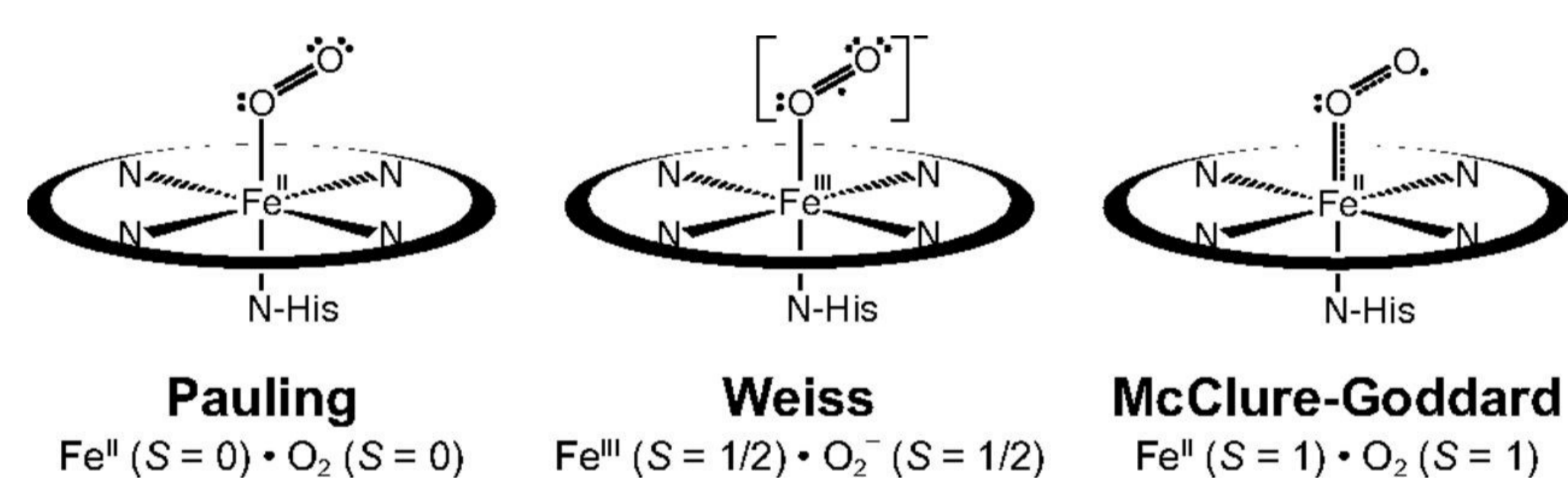
- 100X better energy resolution than CCD or SDD
- 100X better throughput than grating spectrometer

We have commissioned a TES spectrometer at SSRL Beamline 10-1 to study proteins and other dilute samples (attend talk O-85 for more details)



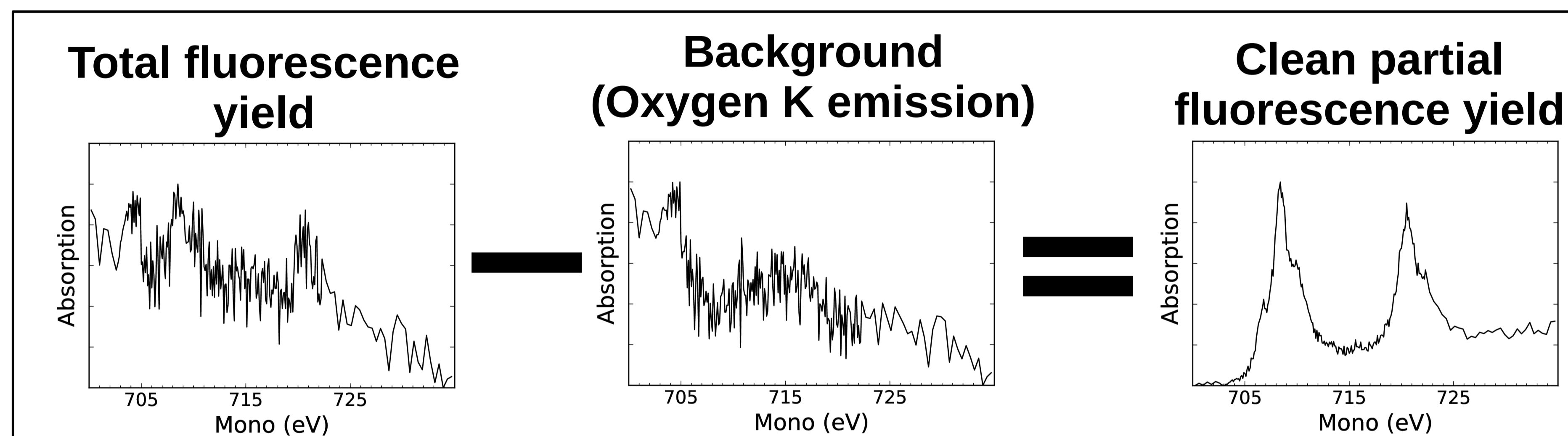
## Measuring hemoglobin spectra with the TES spectrometer

How does hemoglobin bind Oxygen?  
Spectroscopy could settle an 80-year old debate



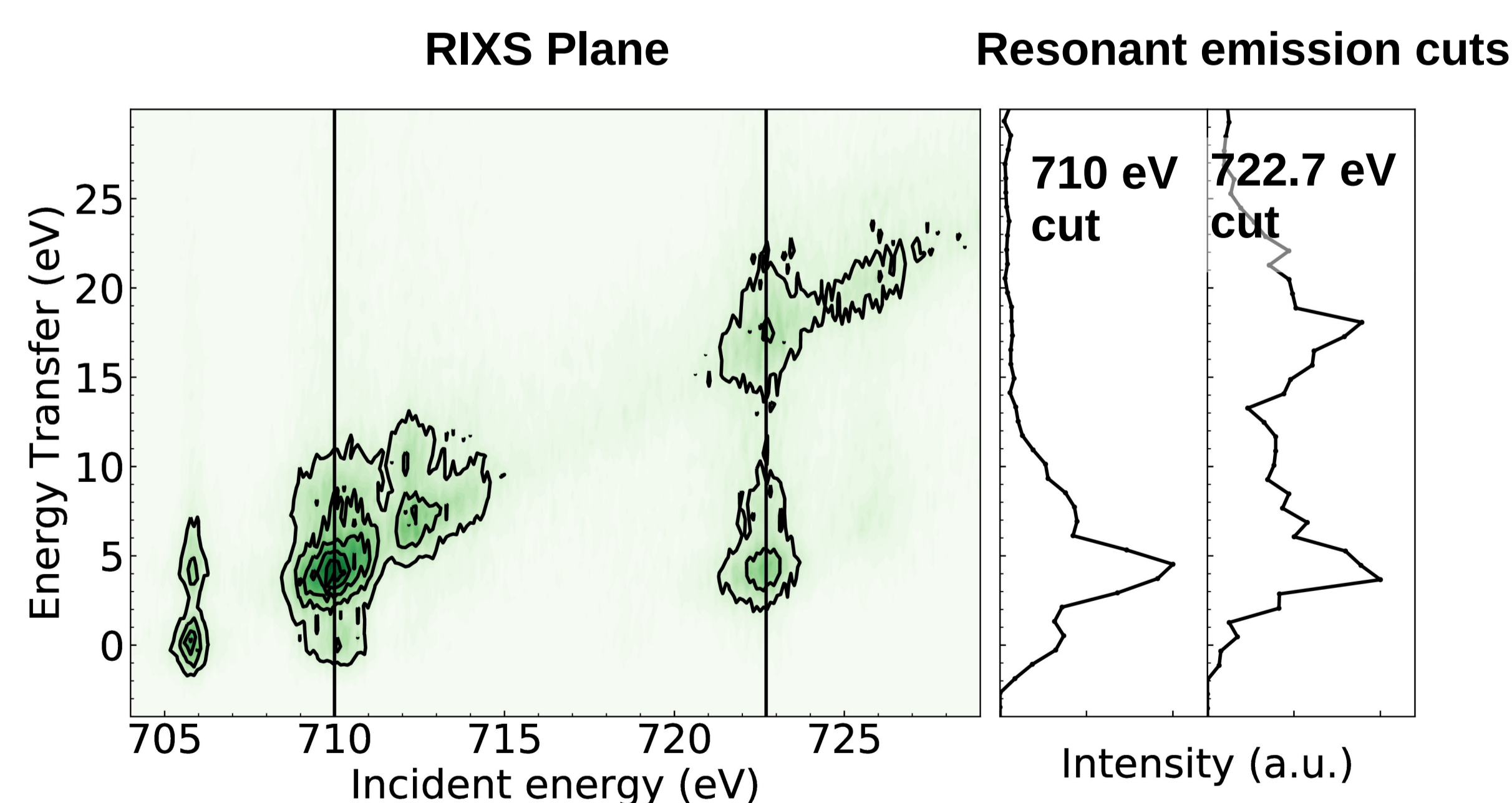
- Three limiting descriptions of Fe-O bond
- Measurement of Oxidation and Spin of central iron atom could settle the debate!
- TES could make definitive measurements

Preliminary TES measurements of hemoglobin show great promise!

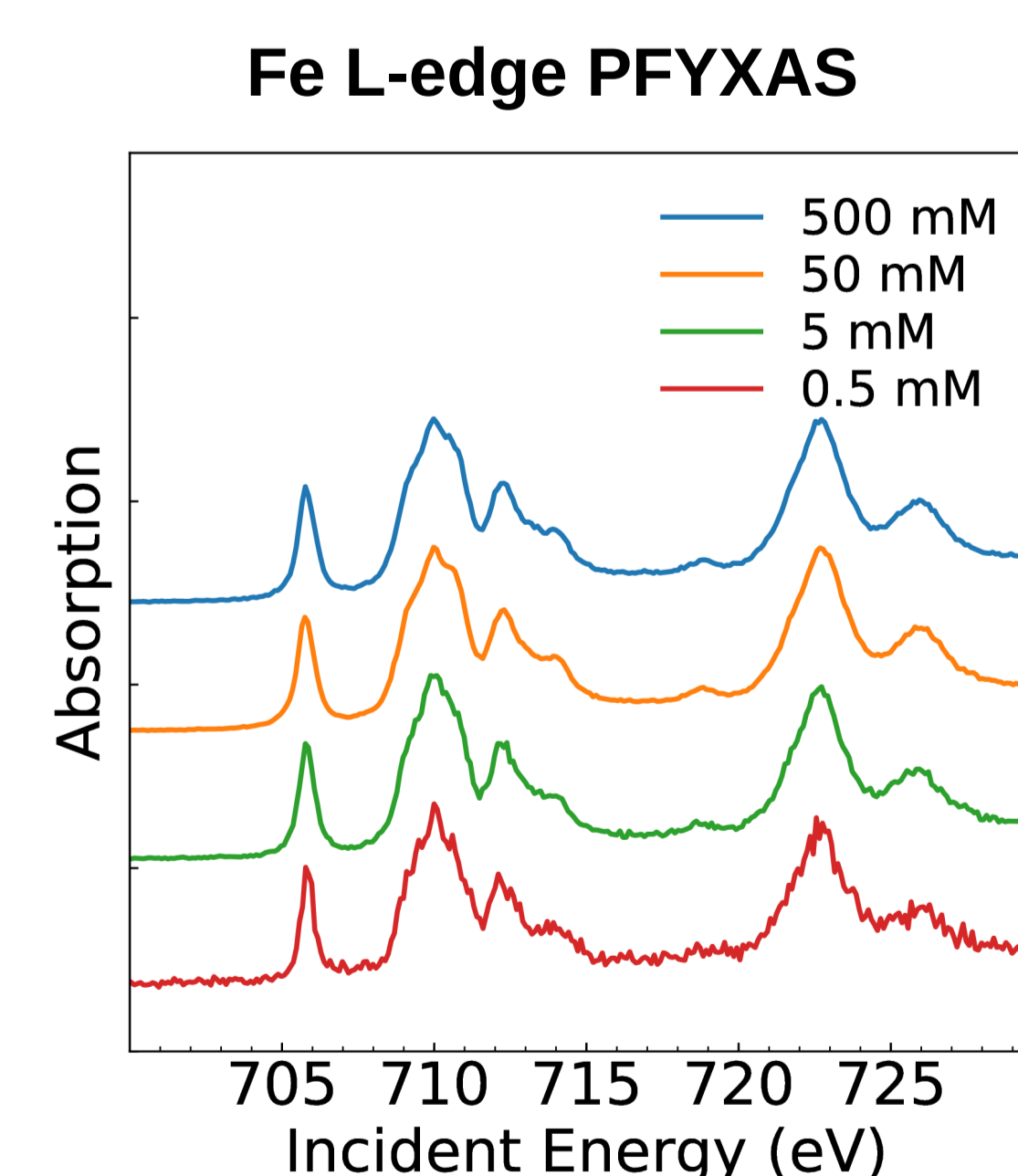


- 15 mM concentration too low for grating spectrometers to measure efficiently
- Overwhelming Oxygen background distorts total fluorescence yield
- TES records a clean PFY signal by windowing background

## Resonant Inelastic X-ray Spectroscopy of dilute Fe<sup>(III)</sup>(CN)<sub>6</sub>



Resonant inelastic X-ray spectroscopy (RIXS) requires good energy resolution and large numbers of photons. The TES spectrometer can make RIXS maps at sample concentrations as low as 5 mM.



TES-recorded PFY spectra demonstrate the power of the SSRL TES spectrometer to probe extremely low sample concentrations.

## Acknowledgements

This work is supported by the Department of Energy, Laboratory Directed Research and Development funding, under contract DE-AC02-76SF00515. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract No. DE-AC02-76SF00515. We gratefully acknowledge support from the DOE Basic Energy Sciences under award #16480-A4001. M.L.B. acknowledges the support of the Human Frontier Science Program. NIST authors acknowledge support from the NIST Innovations in Measurement Science Program and the DOE Office of Basic Energy Sciences. This research was supported by the National Institute of General Medical Sciences of the National Institutes of Health under award number R01GM040392 (E.I.S.) K.D.M. acknowledges the support of a National Research Council Postdoctoral Fellowship.

## Outlook

- Complete removal of background counts
- L-edge XAS spectrum of hemoglobin demonstrated
- XAS of samples as dilute as 0.5 mM demonstrated
- Many more metal-centered proteins and catalysts possible
- Future upgrades push to lower concentration