41 parallel sessions

11 special topic forum

896 Invited Lectures

1230 Oral Lectures

3056 Posters

~ 8000 intendees

Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR

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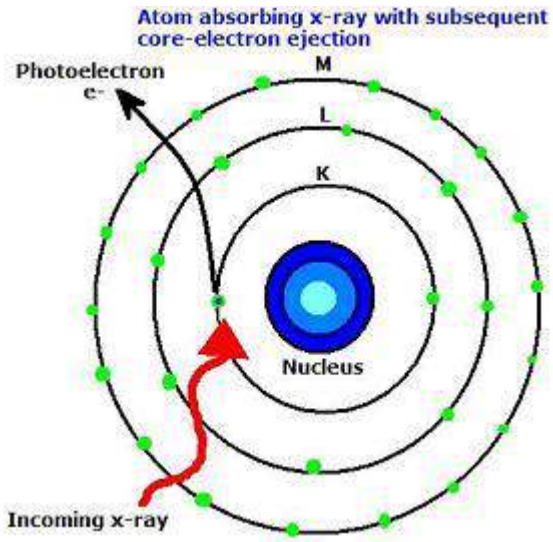
Mechanistic Insight into Transition-Metal Catalysis Revealed by Operando XAS, Raman, EPR and IR

XAS (X-ray absorption spectroscopy) is an element specific method to investigate the bond angles, bond lengths and coordination numbers.



Absorption edges: they correspond to the binding energies of the inner-shell electrons (K, L, M..).

Each chemical element has specific, well-defined binding energies

XAS spectrum can be divided into different parts based on the energy range of the X-ray beam compared to the absorption edge

1. Pre-edge: no ionisation occurs
2. XANES (X-ray Near Edge Structure): $E < E^0+10$ eV
3. NEXAFS (Near-Edge X-ray Absorption Fine Structure): $E^0+10<E<E^0+50$ eV
4. EXAFS (Extended X-ray Absorption Fine Structure): $E > E^0+50$ eV

http://www.szfki.hu/~nphys/rmc++/EXAFS.htm

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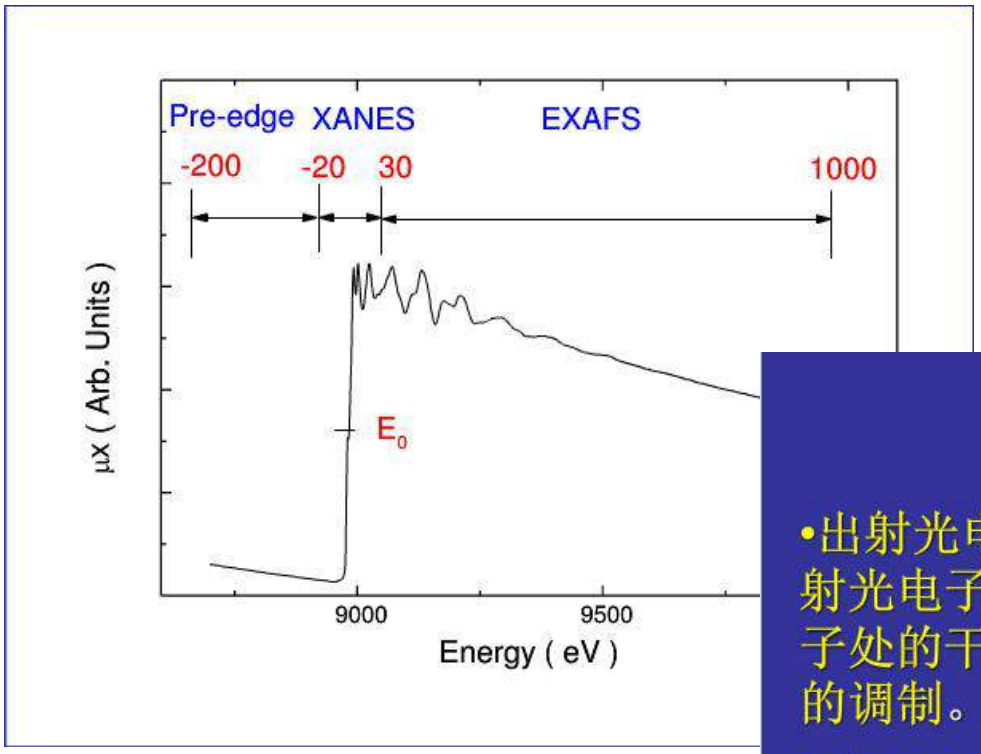
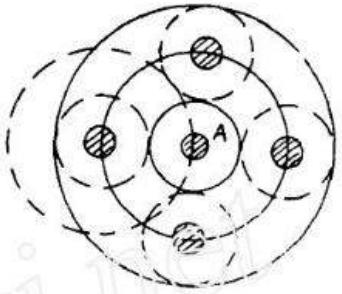


According the fine structure of the spectrum, XAFS can get the information about the neighboring atoms.

产生的物理机制

•出射光电子波与背散射光电子波在吸收原子处的干涉对吸收谱的调制。

干涉是由出射波与散射波的相位差引起的，与入射波的强弱、近邻原子的种类及数目N、以及吸收原子到近邻原子的距离R有关。所以，通过XAFS可得到近邻原子的信息。



图二　表示光电子末态|f>的组成。阴影圆表示原子，实线圆表示原子A吸收x光子产生光电子的出射波，虚线圆表示邻近原子的散射波。

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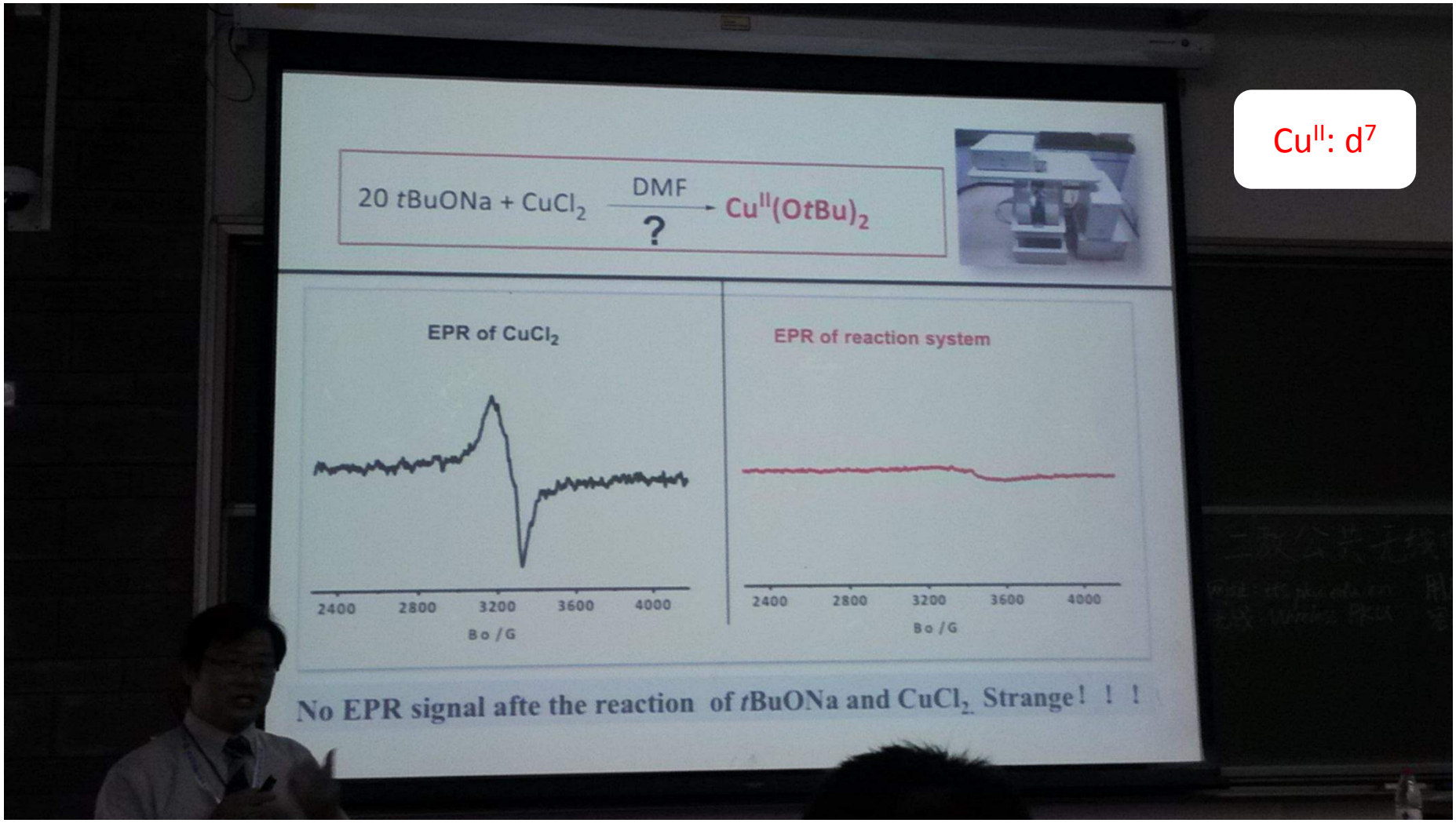
Electron paramagnetic resonance (EPR)

A technique for studying materials with unpaired electrons.



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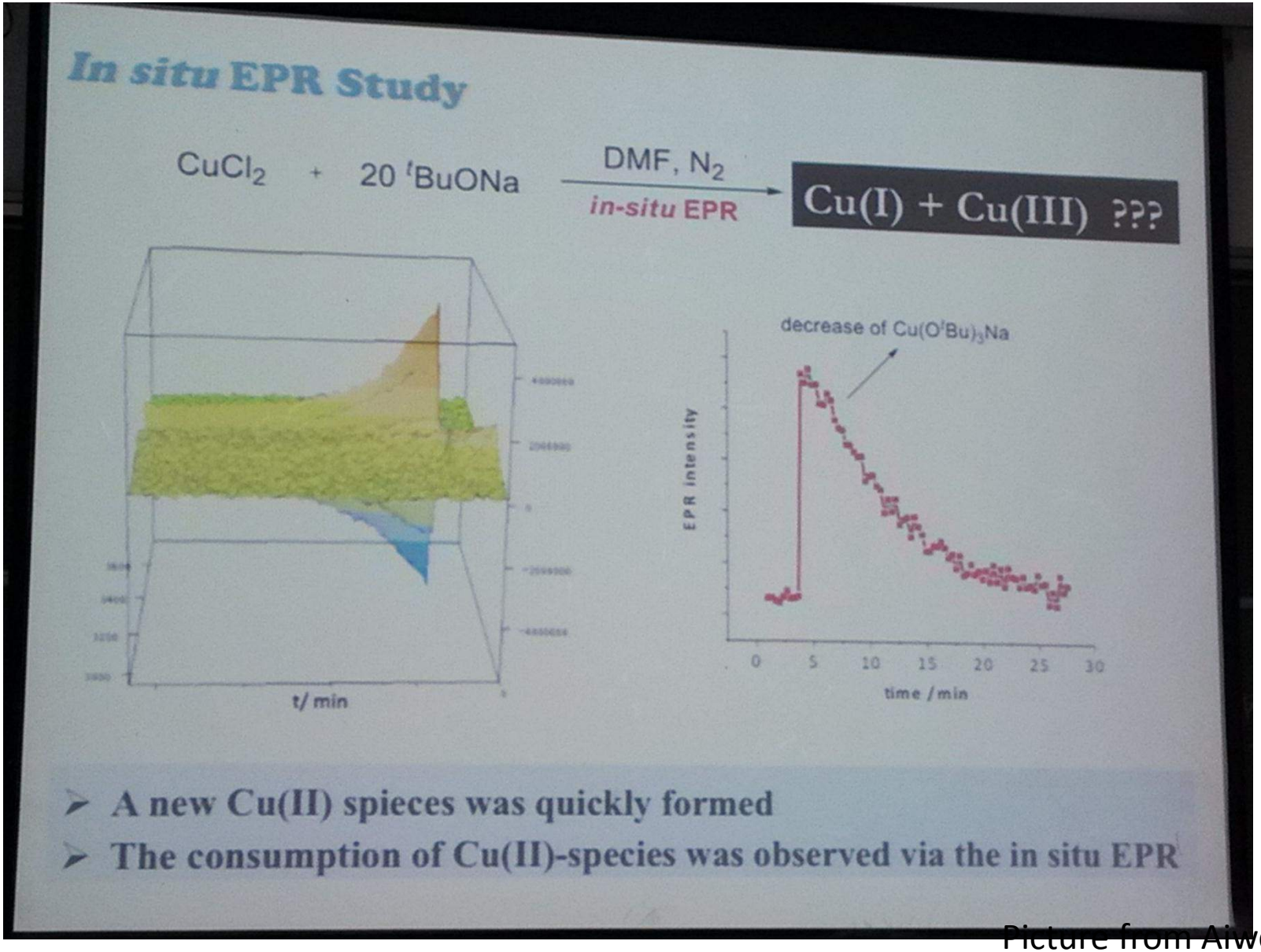

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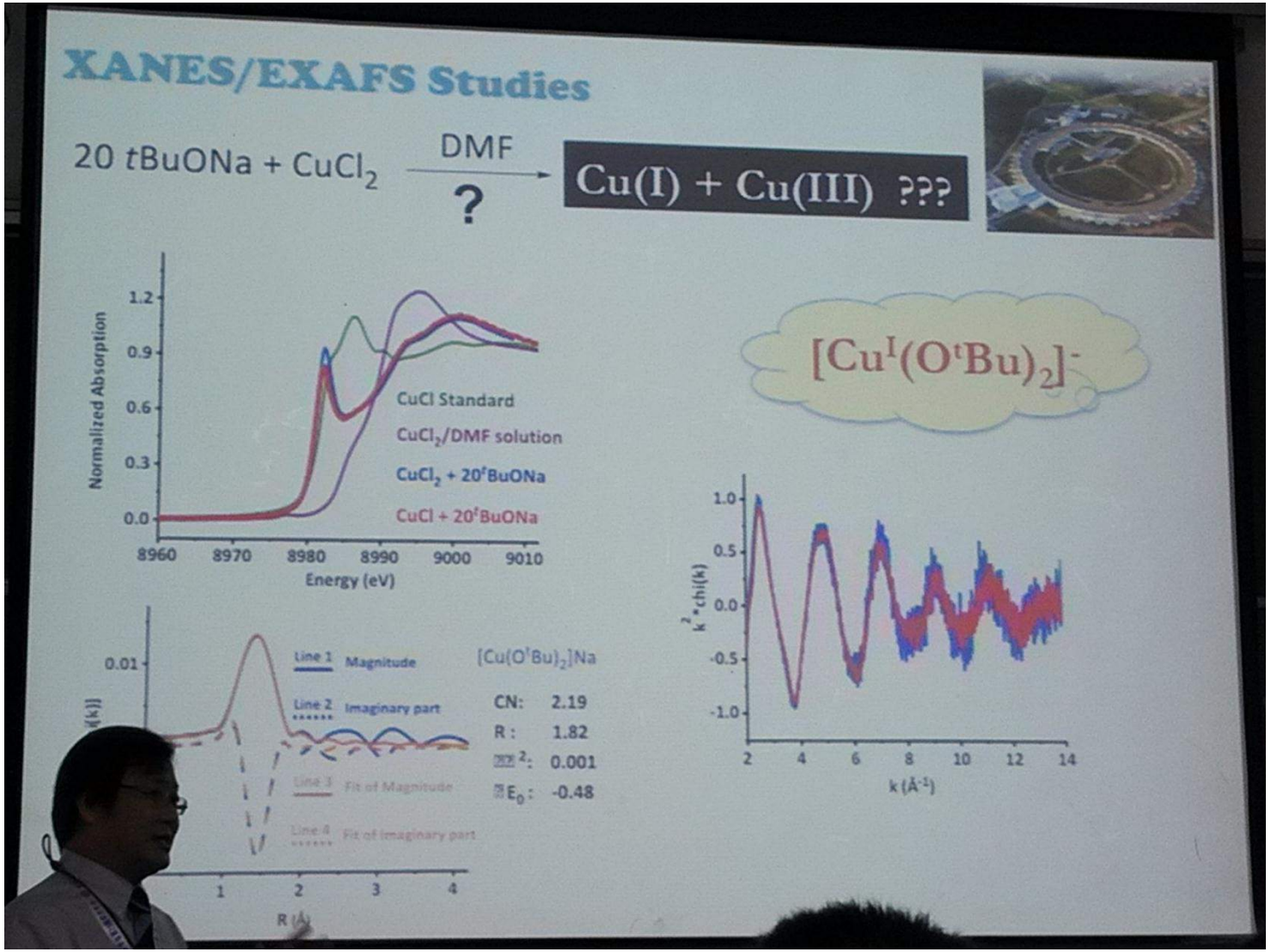

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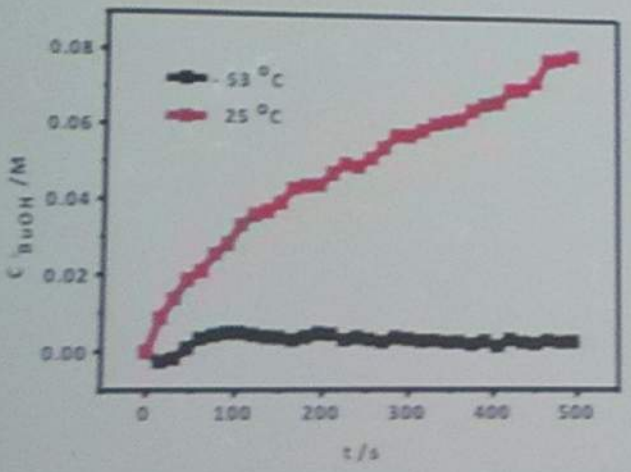
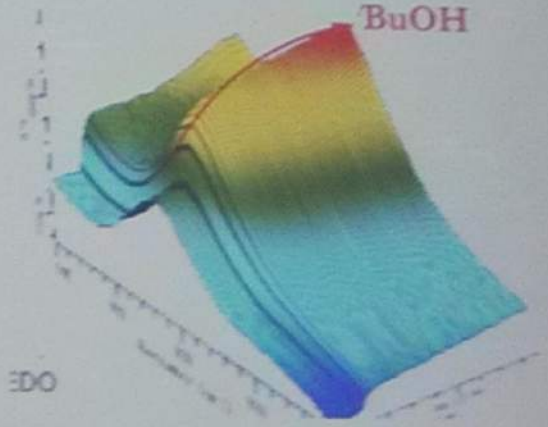
Operando IR Study

$$Cu^{II}(O^tBu)_3Na \xrightarrow[25^\circ C,\ N_2]{DMF} Cu^{I}(O^tBu)_2Na + \ ?$$

Kinetic profiles of the reduction





The kinetic profiles of 25 °C and -53 °C were shown. No reduction occurs at -53 °C

Picture from Aiwen Lei

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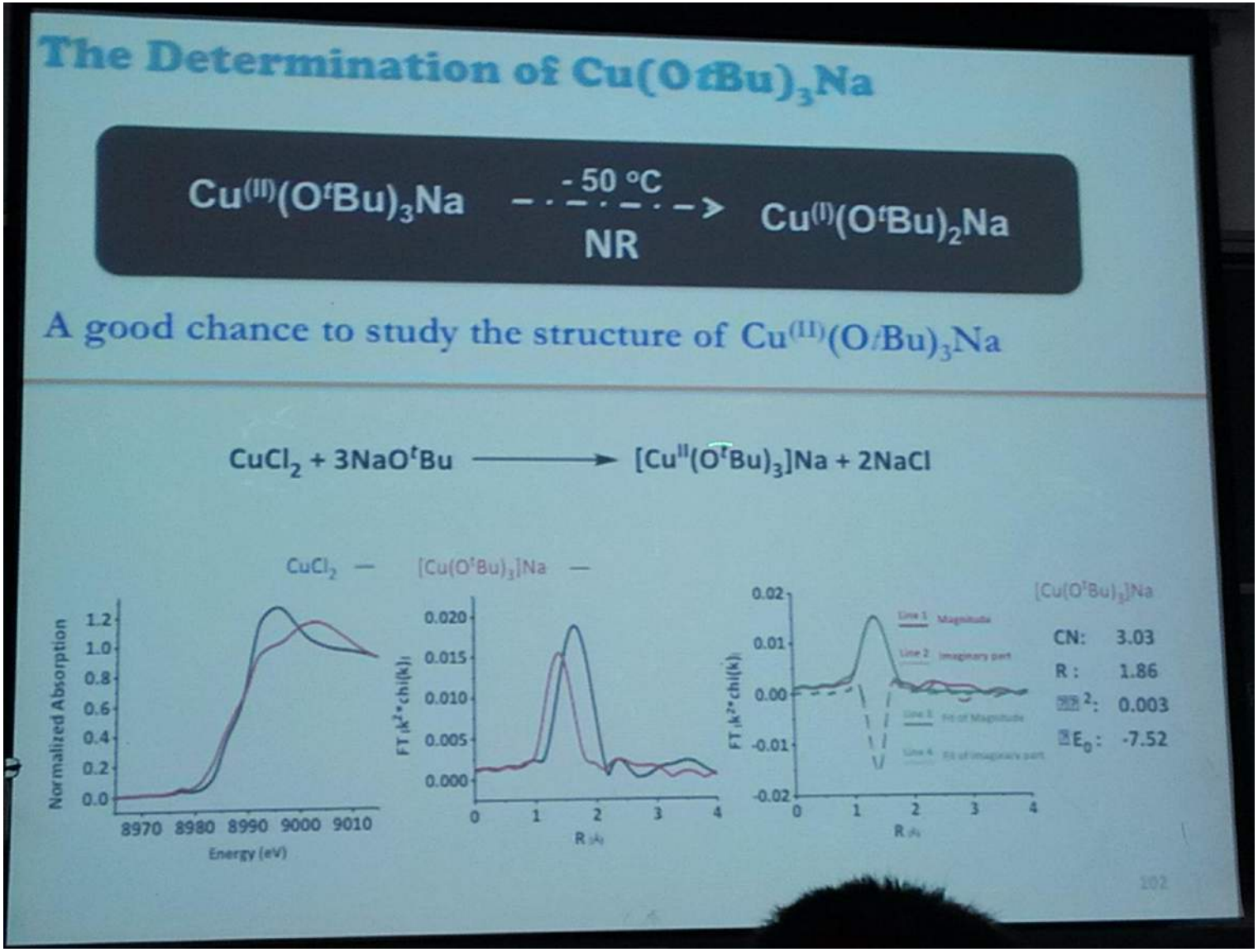

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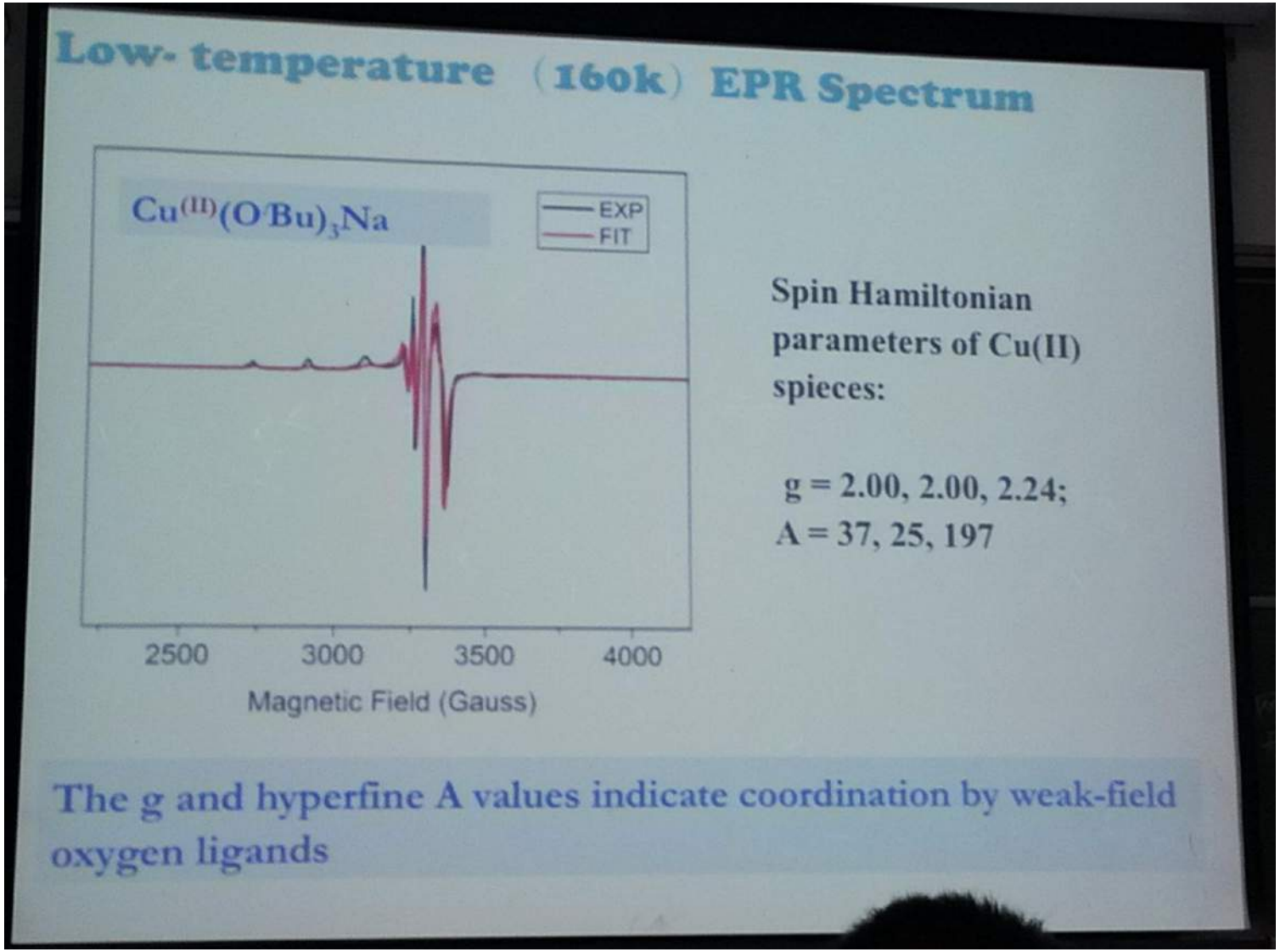

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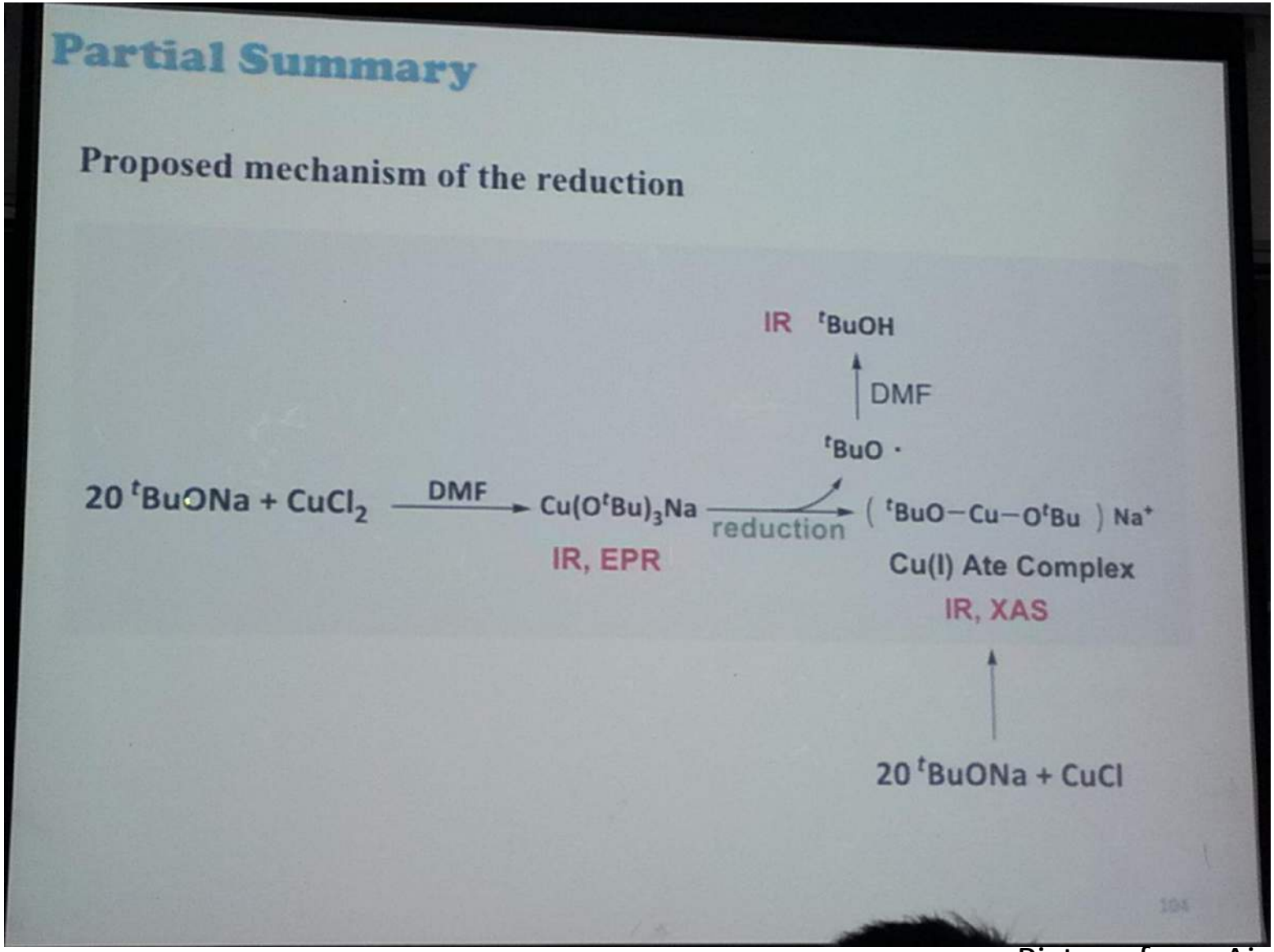

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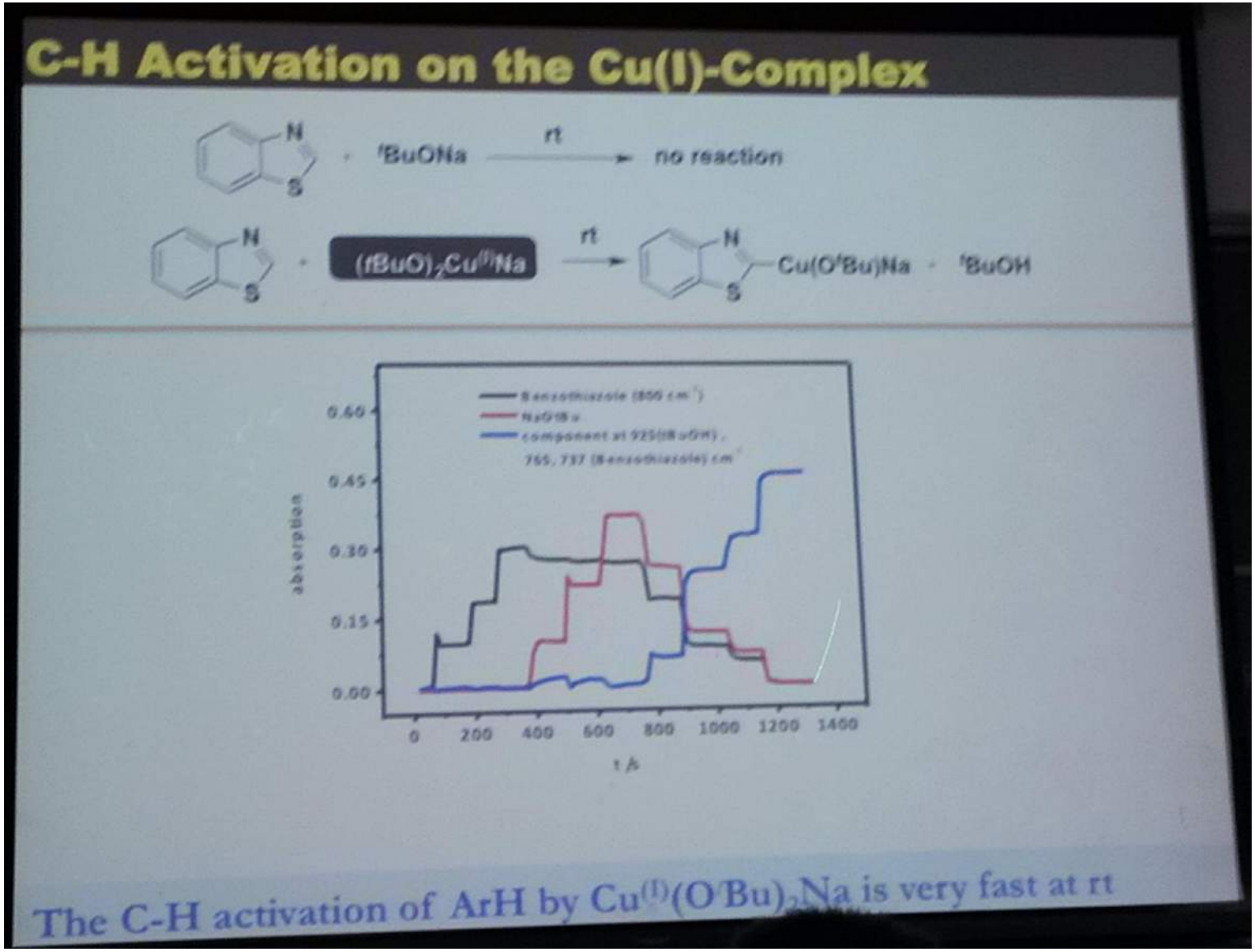

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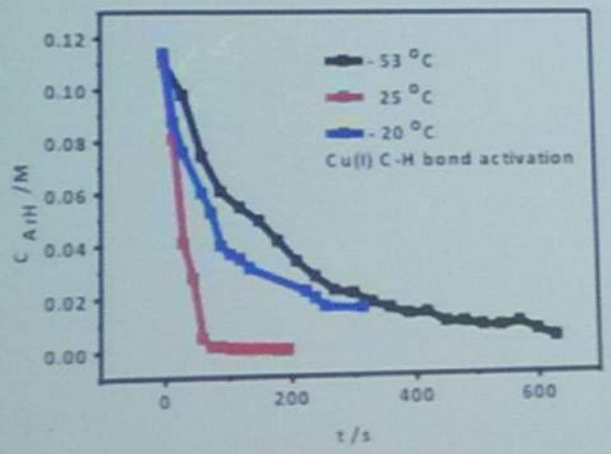
Kinetic Profiles

$$Cu^{I}(O^{t}Bu)_2Na + ArH \xrightarrow[DMF,\ N_2]{-50\ ^\circ C} ArCu^{I}(O^{t}Bu)Na + {}^{t}BuOH$$



$v = k[Cu^{(I)}(OtBu)_2Na][ArH]$

$k = 3.2*10^{-2}$ $mol^{-1}Ls^{-1}$ @ -53 °C

$k = 4.8*10^{-2}$ $mol^{-1}Ls^{-1}$ @ -20 °C

The C-H activation could be completed within 10 mins @ -53 °C

Picture from Aiwen Lei

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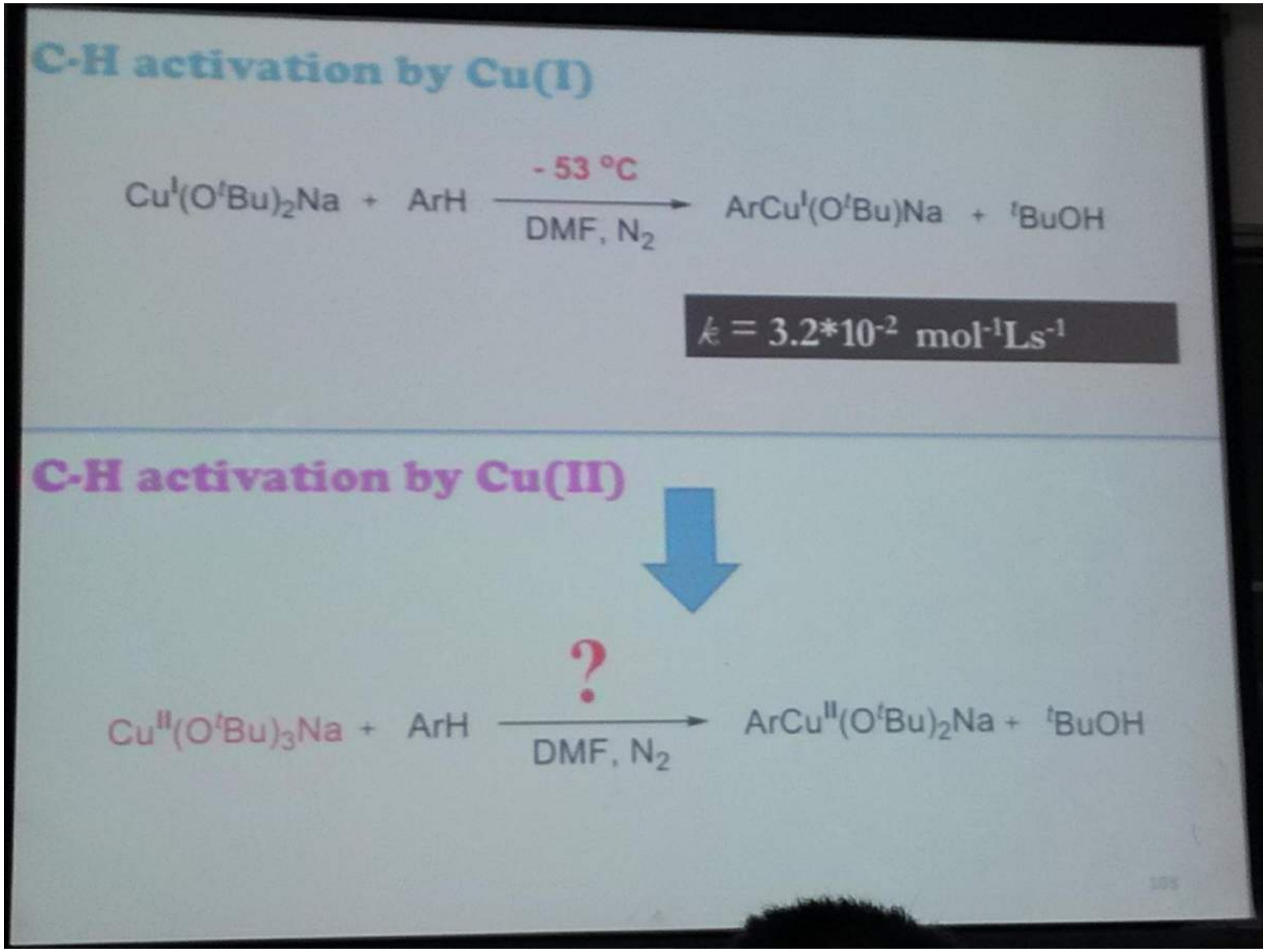

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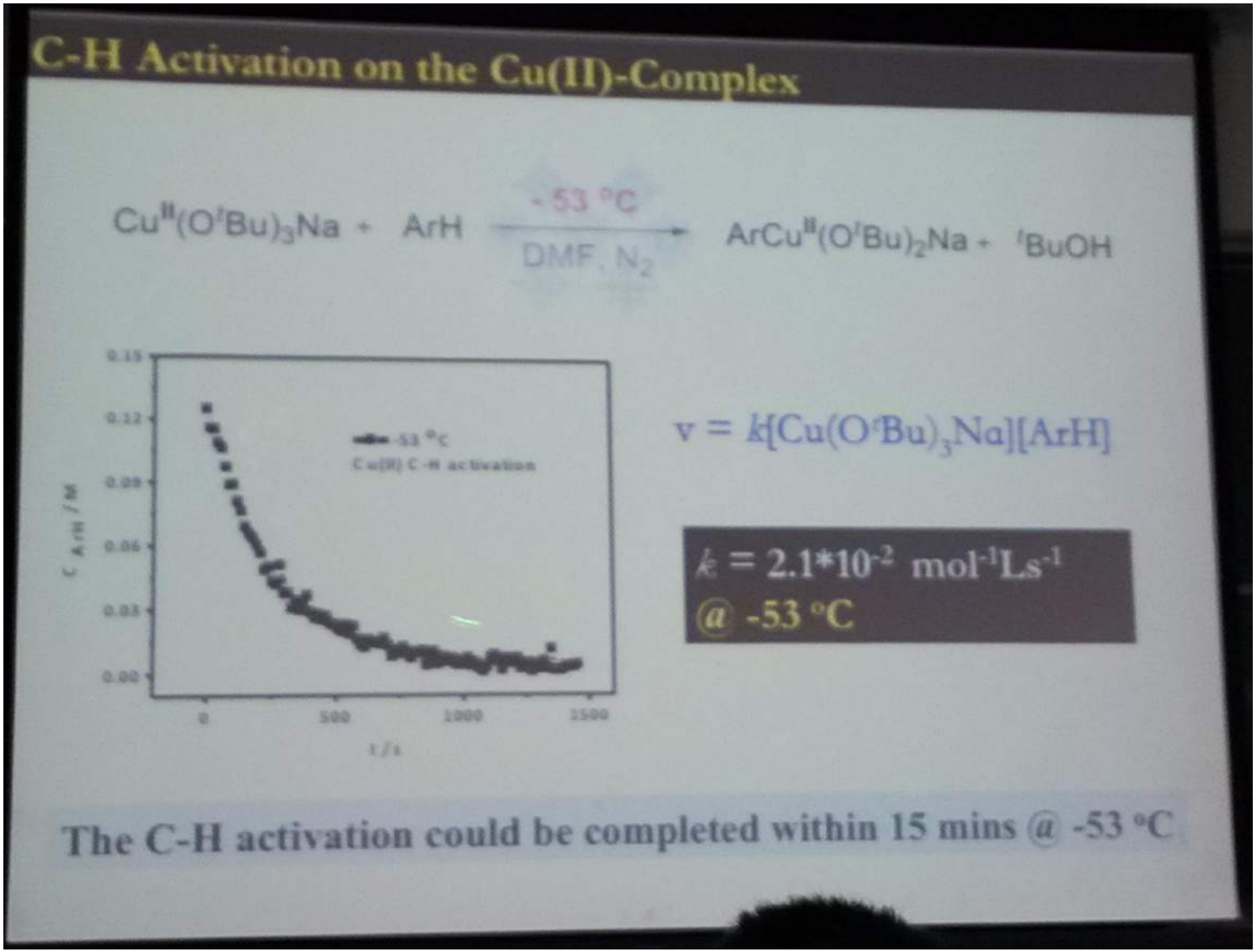

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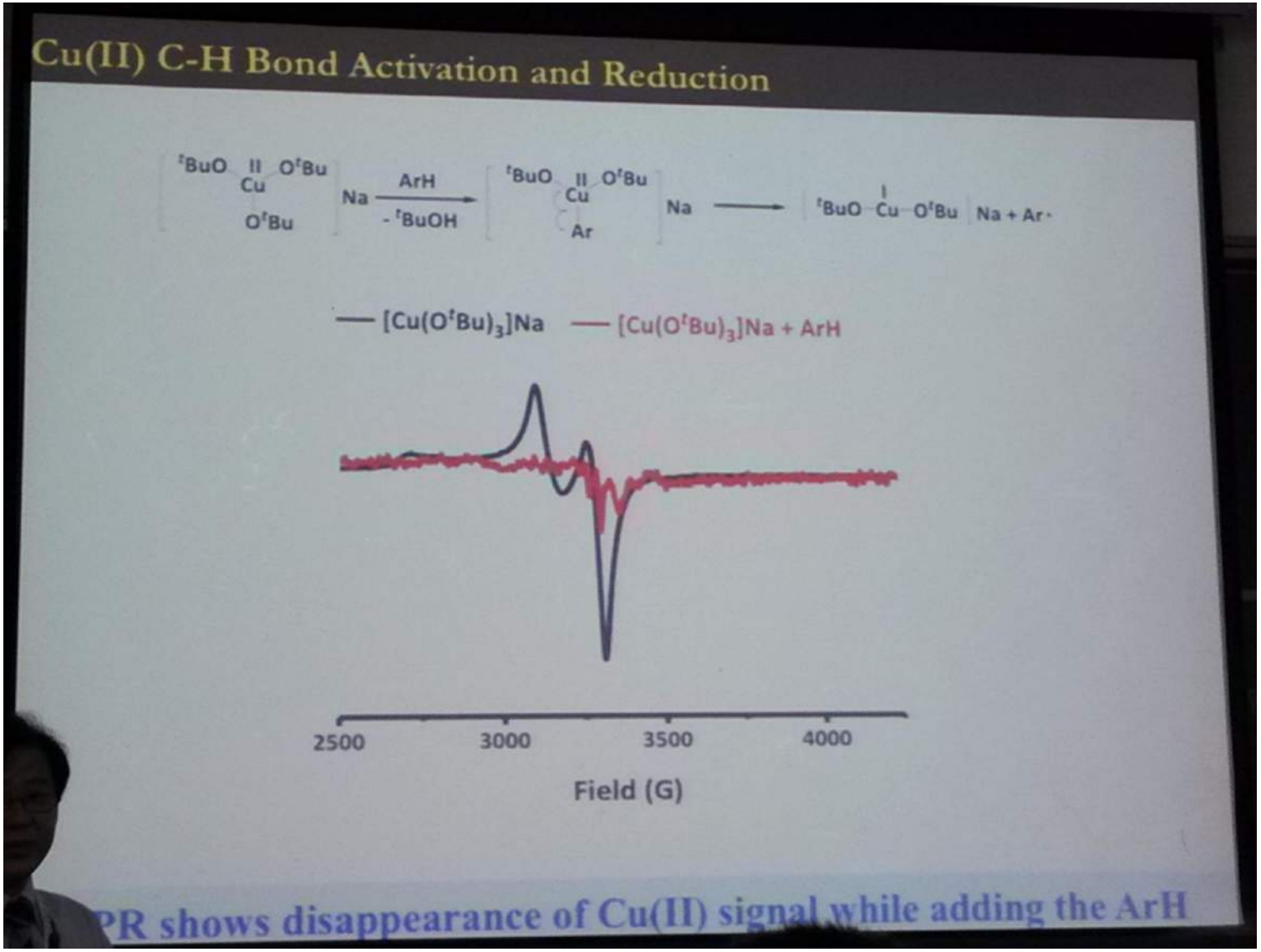

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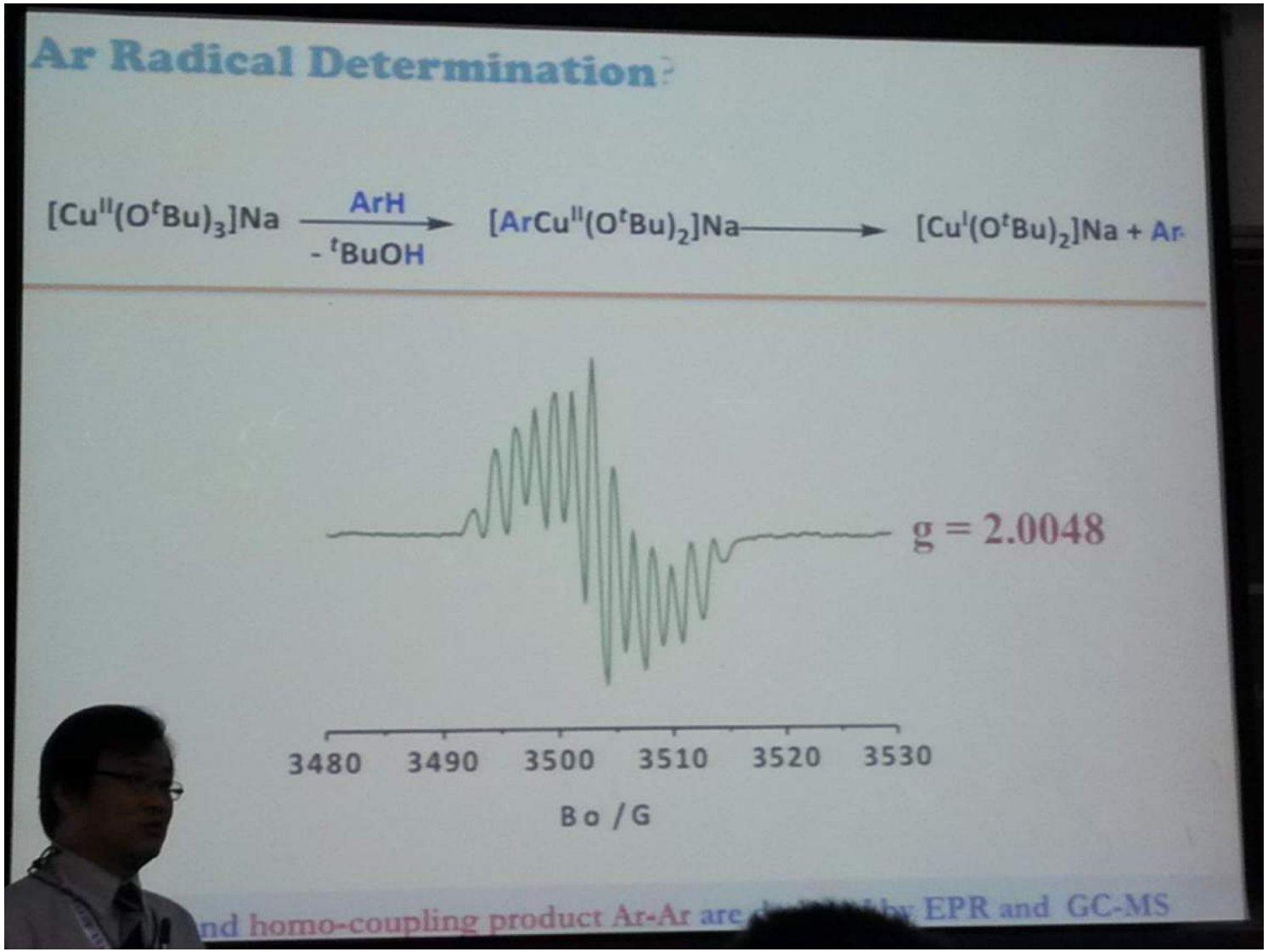

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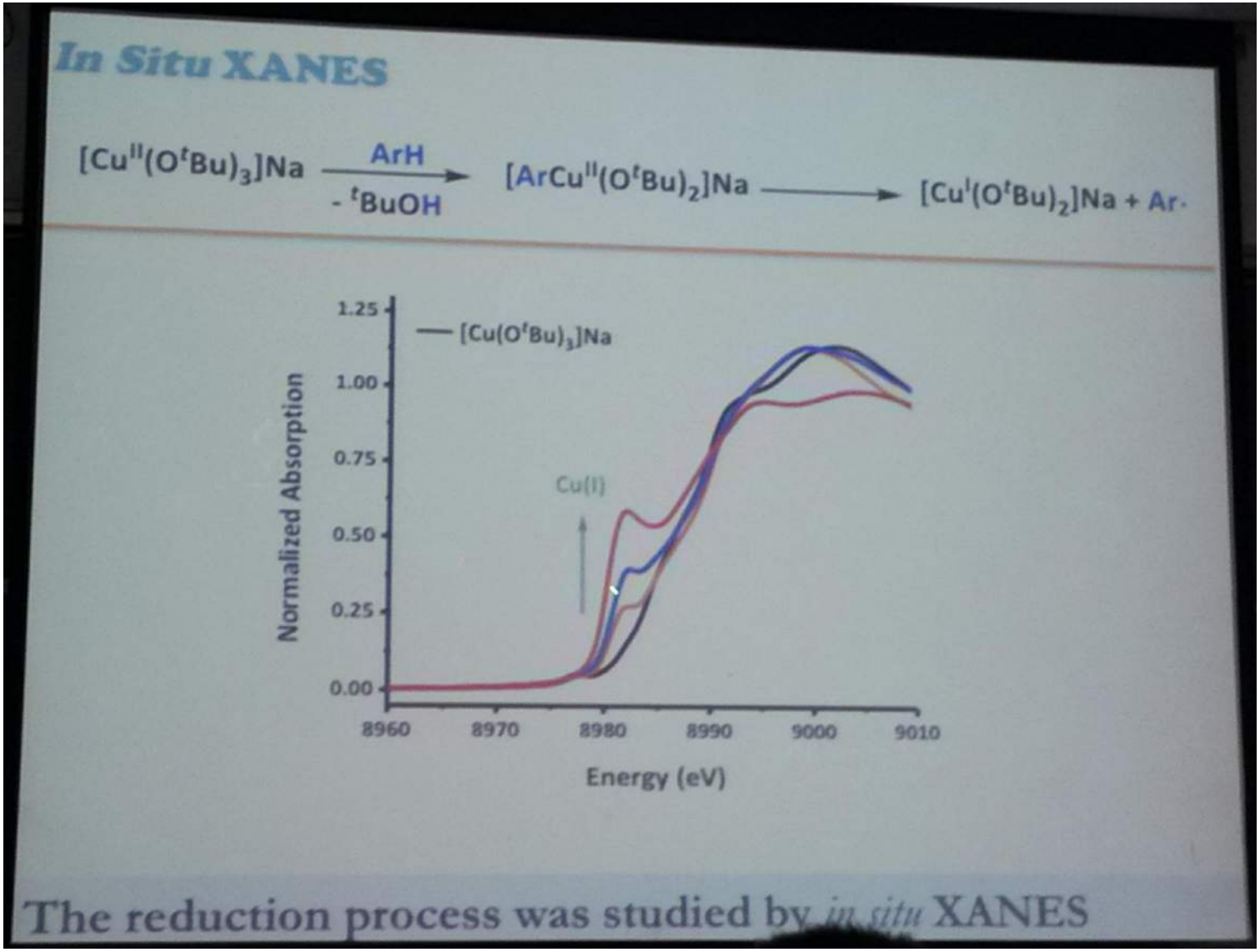

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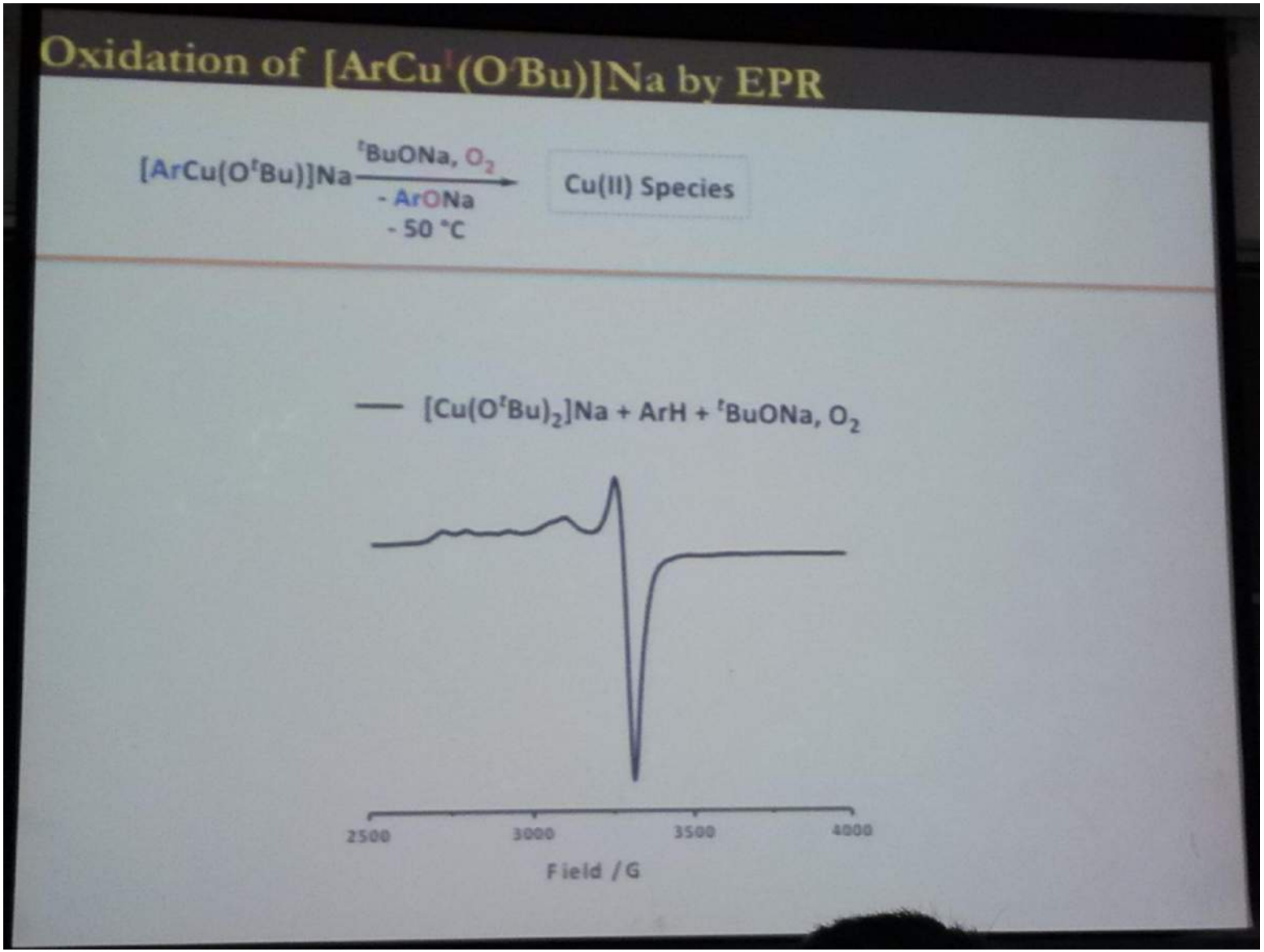

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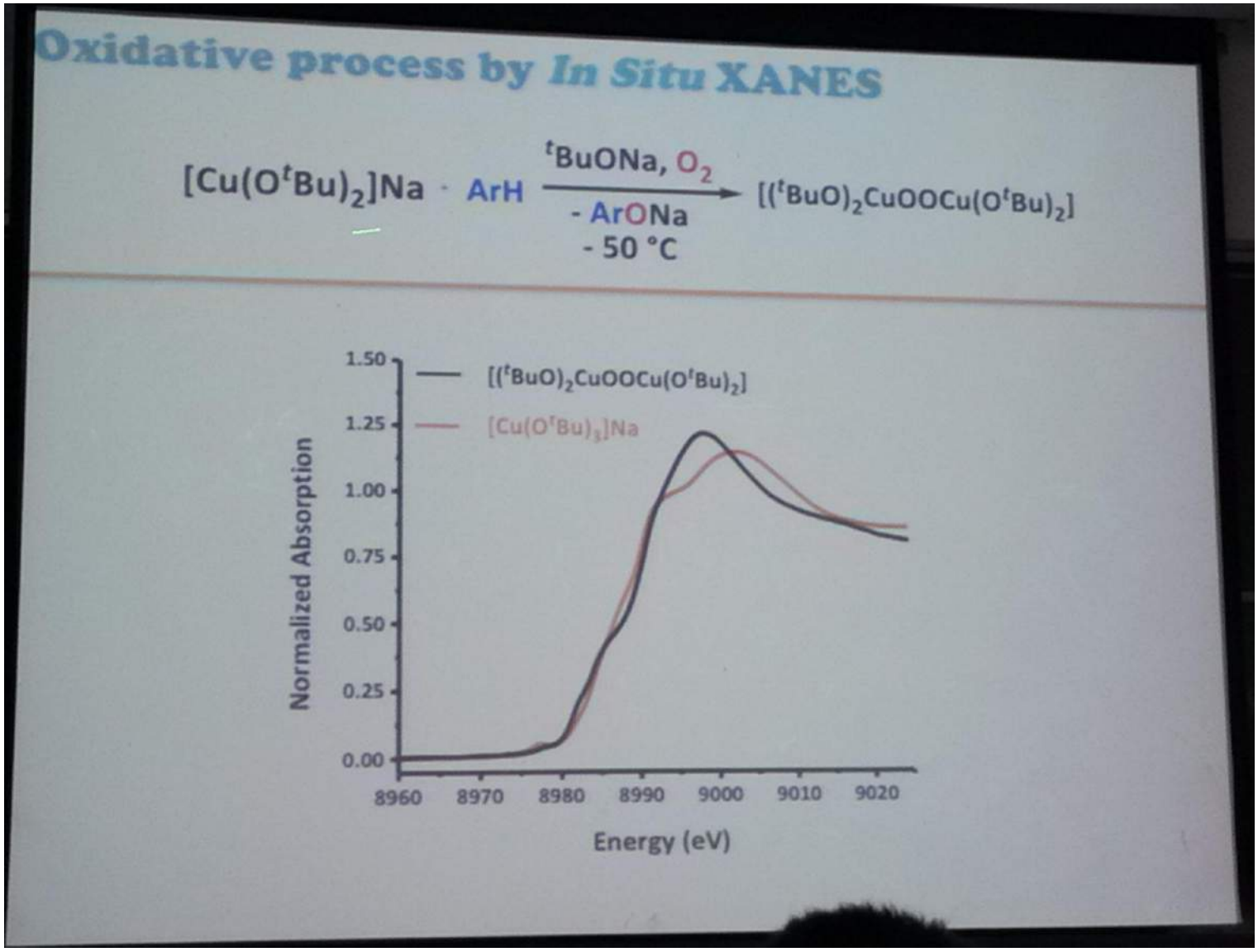

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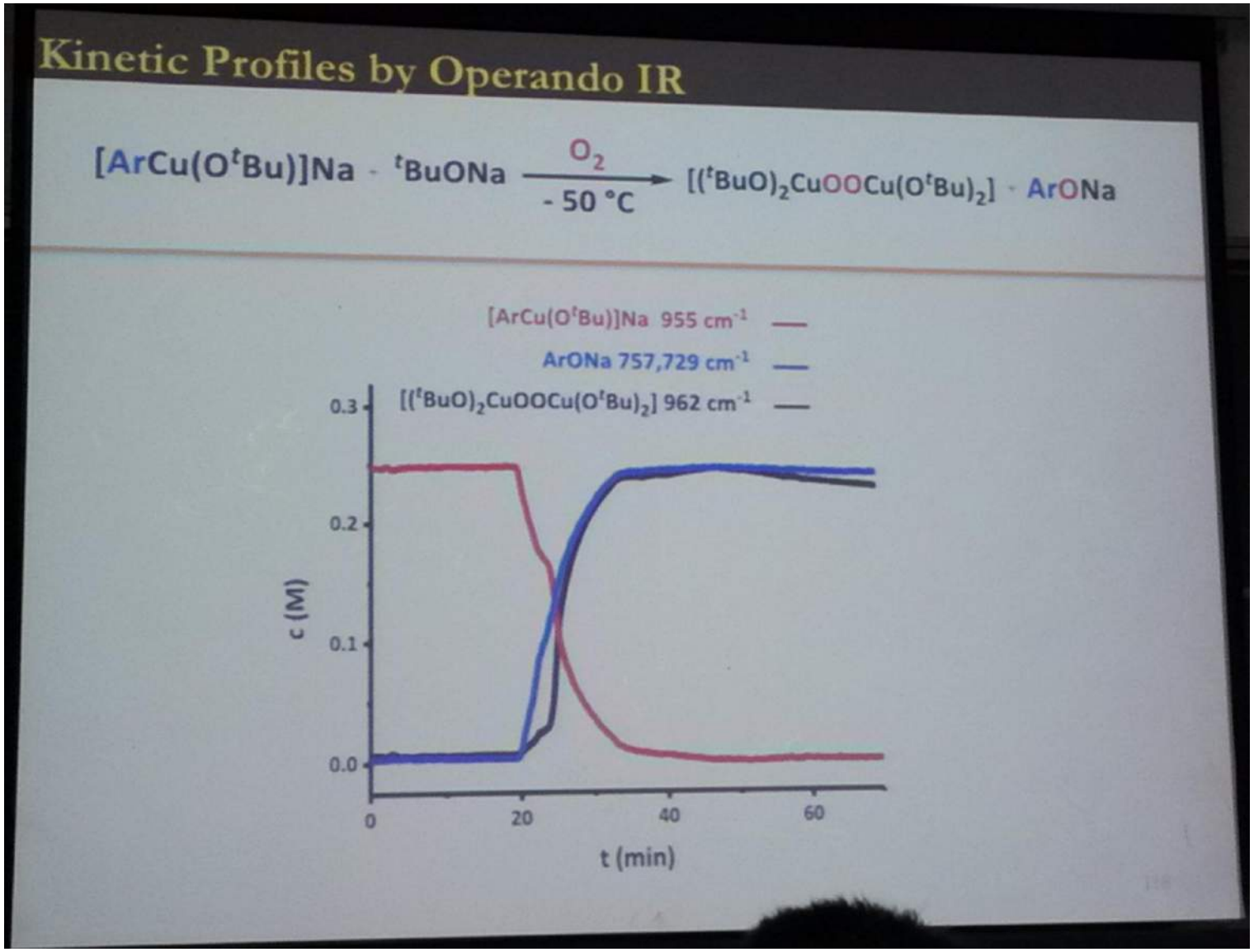

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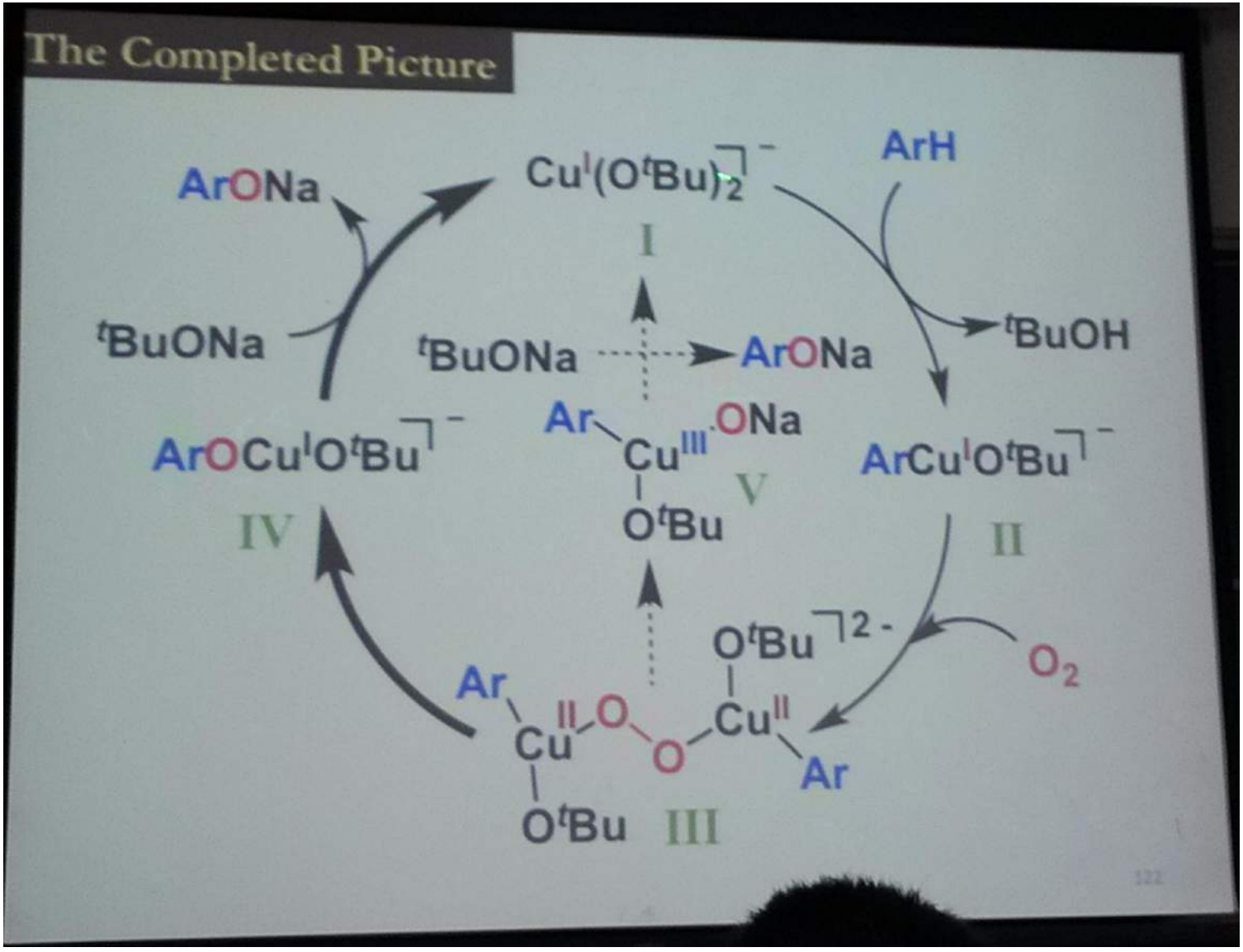

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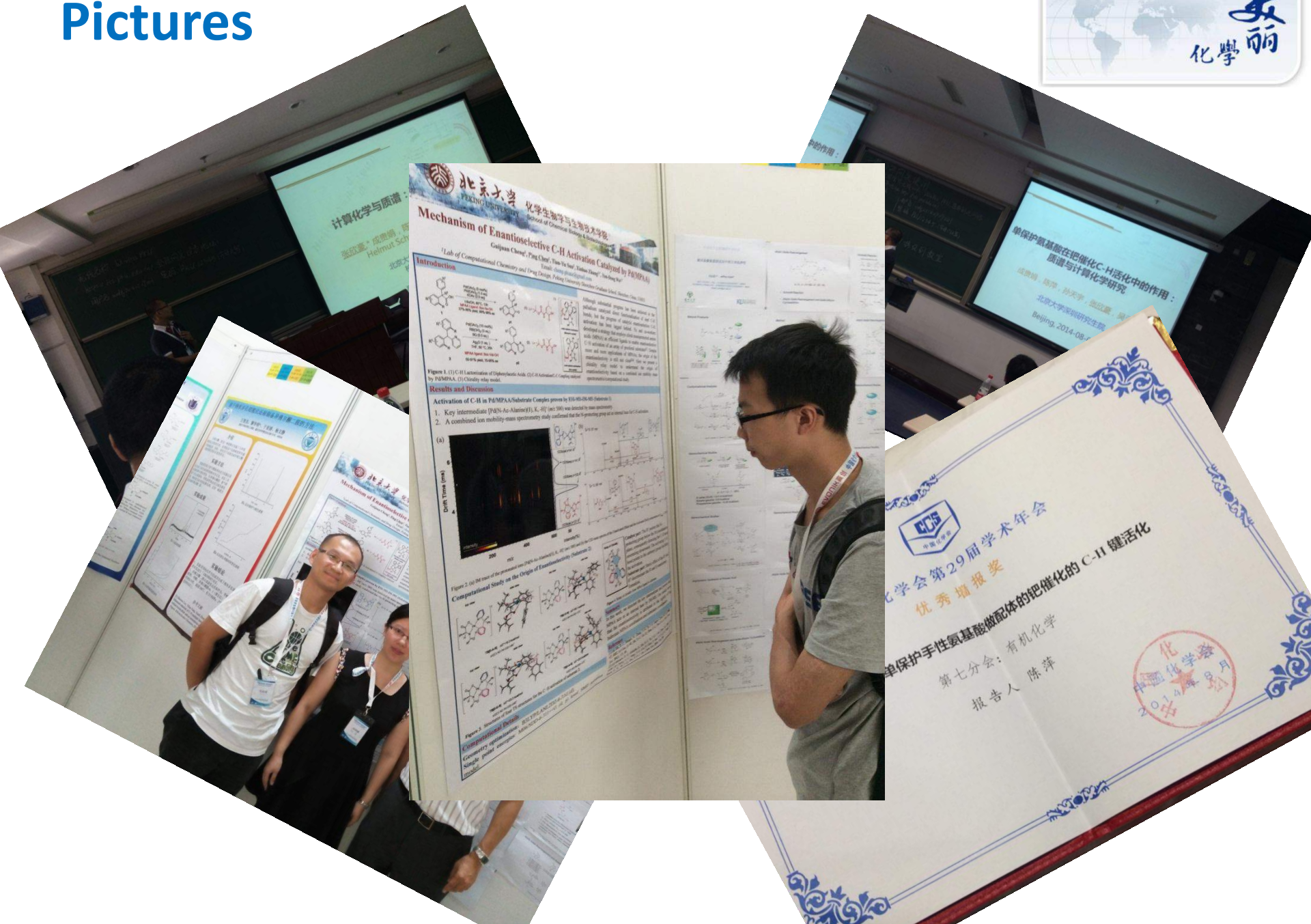
Pictures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Mechanism of Enantioselective C-H Activation Catalyzed by Pd/MPAA
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Results and Discussion
Computational Study on the Origin of Enantioselectivity
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Thanks for you attention!