SLAC-WP-124

Dipole Alignment at the Carbon Nanotube and Methyl Ammonium Lead Trihalide Perovskite Interface

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Office of Science, Science Undergraduate Laboratory Internship (SULI) Program

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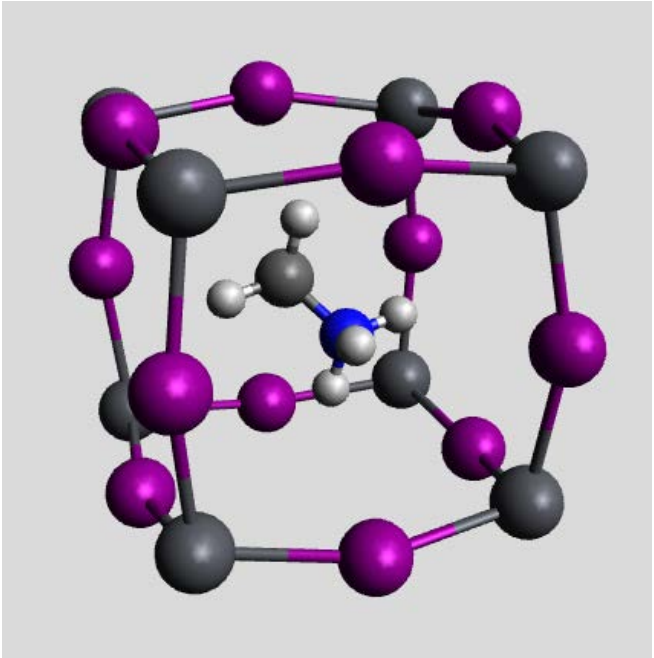
Abstract

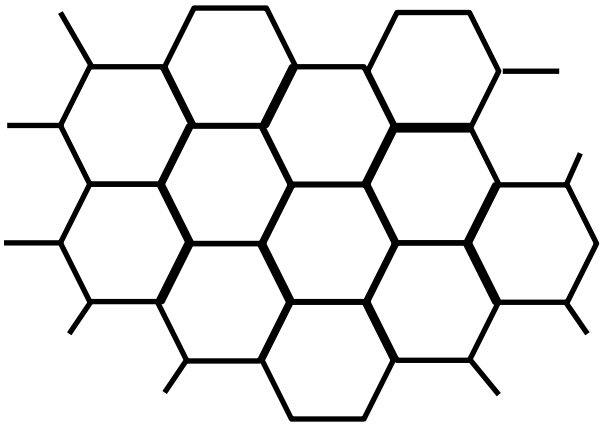
This work correlates resonant peaks from first principles calculation on ammonia (NH_3) Nitrogen 1s x-ray absorption spectroscopy (XAS) within the methyl ammonium lead iodide perovskite ($CH_3NH_3PbI_3$), and proposes a curve to determine the alignment of the methyl ammonium dipole if there exists angular dependence. The Nitrogen 1s XAS was performed at varying incident angles on the perovskite with and without a carbon nanotube (CNT) interface produced from an ultrasonic spray deposition. We investigated the peak contribution from PbI_2 and the poly(9,9-dioctylfluorene-2,7-diyl) with bipyridine (PFO-BPy) wrapped around the CNT, and used normalization techniques to better identify the dipole alignment. There was angular dependence on samples containing the CNT interface suggesting an existing dipole alignment, but there was no angular dependence on the perovskite samples alone; however, more normalization techniques and experimental work must be performed in order to ensure its validity and to better describe its alignment, and possible controlling factors.

What are Perovskites and Carbon Nanotubes (CNT)?

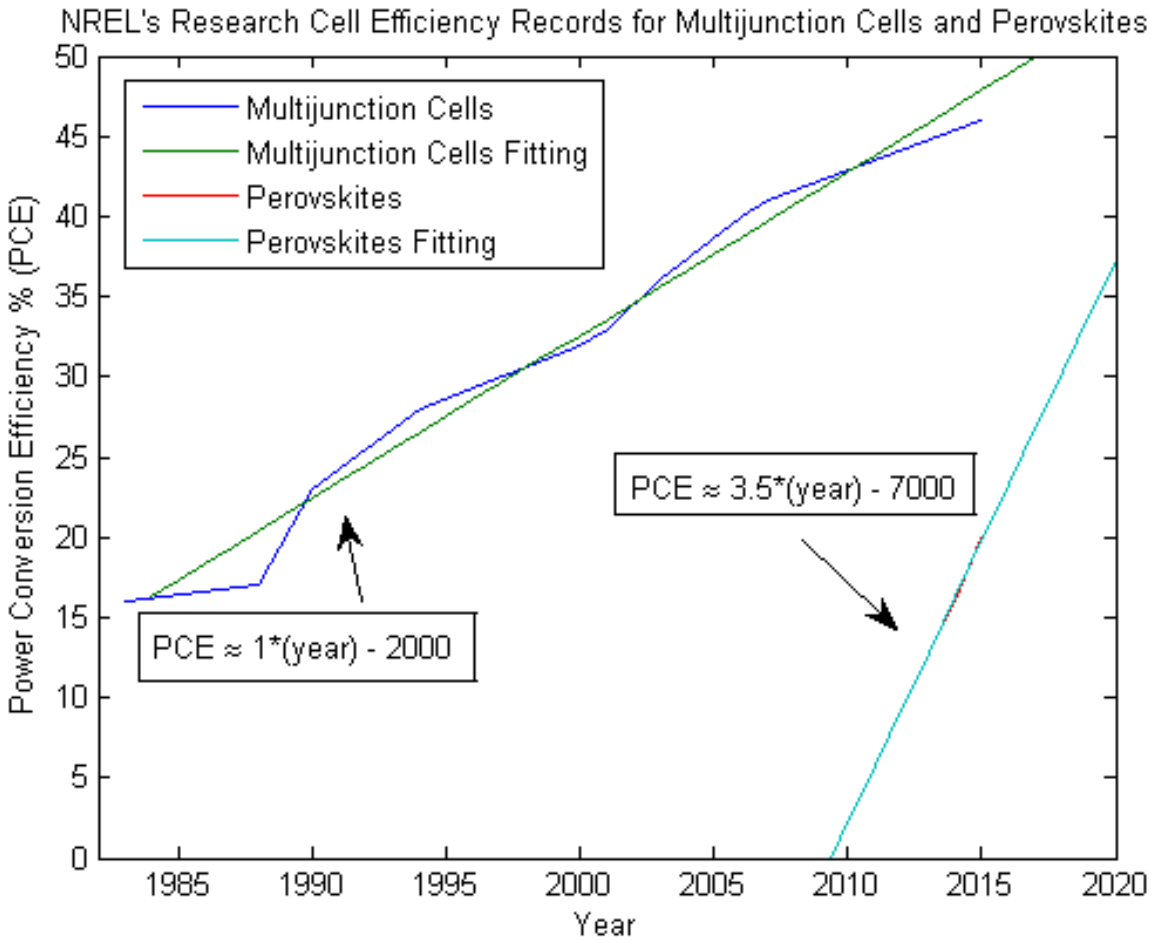
- Perovskite is a molecule with a Body Center Cell (BCC) structure with the form ABX_3, where A is the largest component of the cell.
- Our Perovskite of interest is Methyl Ammonium Lead Trihalide ($CH_3NH_3PbX_3$, X = I or Br), and the Methyl Ammonium is in the center of the molecule / cell.



- A Carbon Nanotube (CNT) is a “rolled up” sheet of graphene, which is a single layer of Carbon.



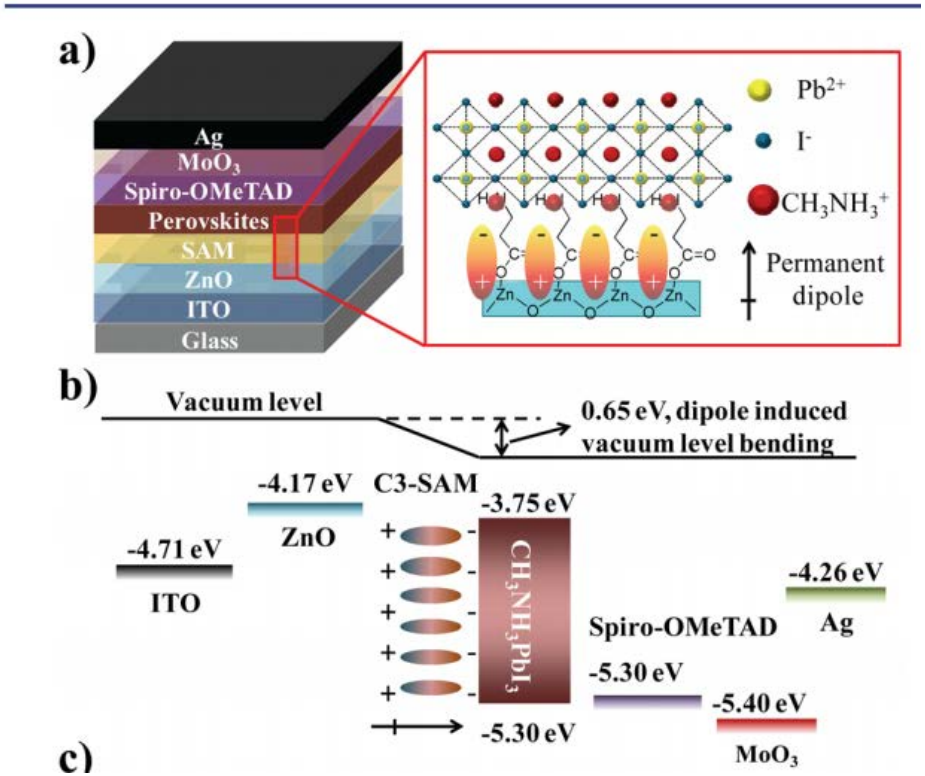
Why Perovskite?



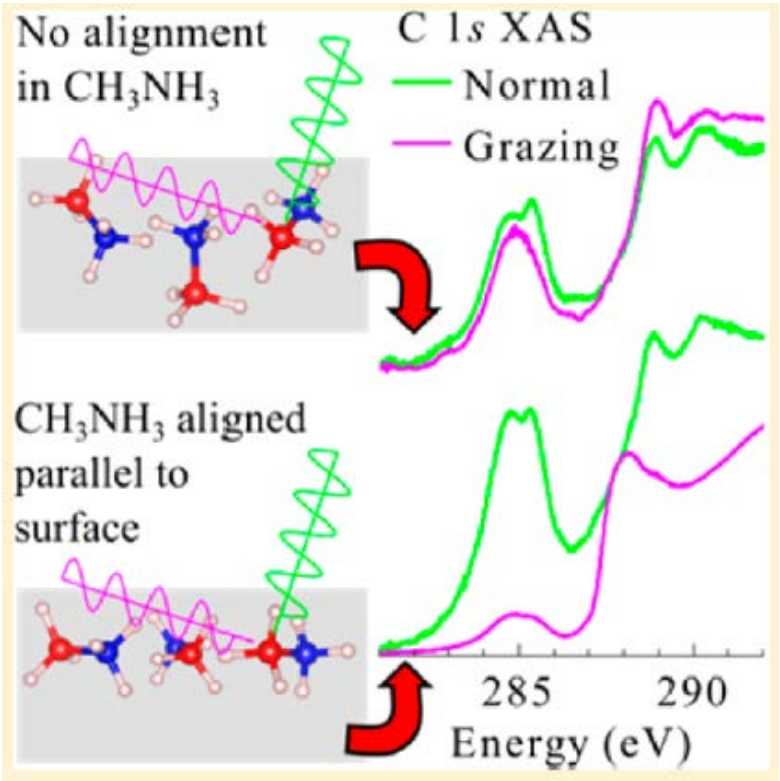
- **Faster**
- **Easier**
- **Cheaper**

Experimental Motivation

- Controlled energy levels using a Carbon Nanotubes on Perovskite interface
- Angular dependence on Perovskite material
- Role of the $CH_3NH_3^+$ dipole **has been inferred** in previous papers, but **has not been proven**



J. Am. Chem. Soc. 137, 2674 (2015).

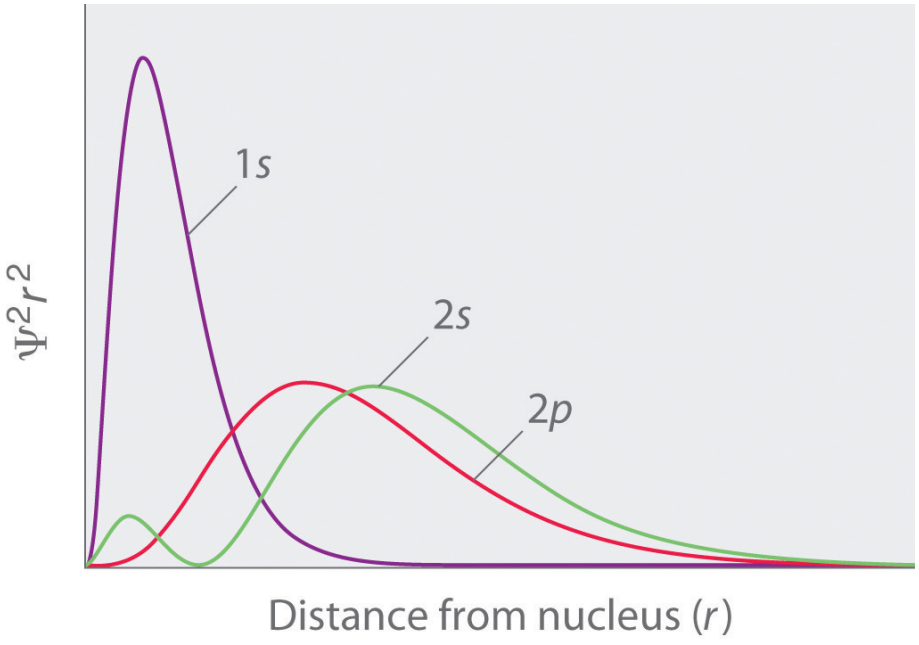


J. Phys. Chem. Lett 5, 2863 (2014).

Our Strategy: X-Ray Absorption Spectroscopy (XAS) and First Principles

$$XAS = \langle \psi_{final} | E \cdot r | \psi_{1s} \rangle$$

- $\langle \psi_{2s} | E \cdot r | \psi_{1s} \rangle = 0$
- $\langle \psi_{2p} | E \cdot r | \psi_{1s} \rangle \neq 0$

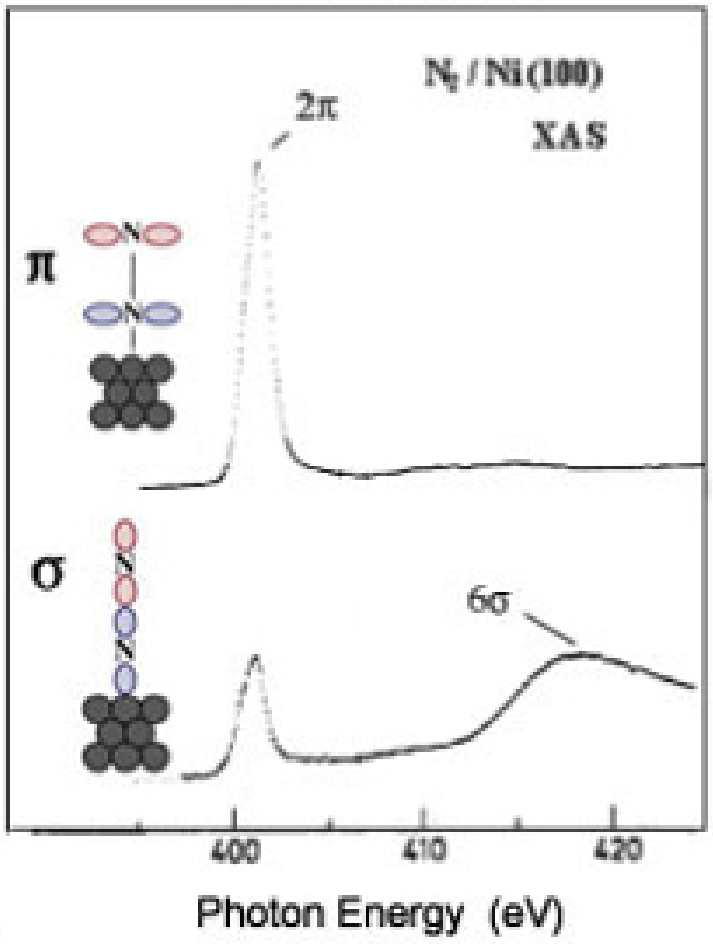


Dipole Selection Rule:

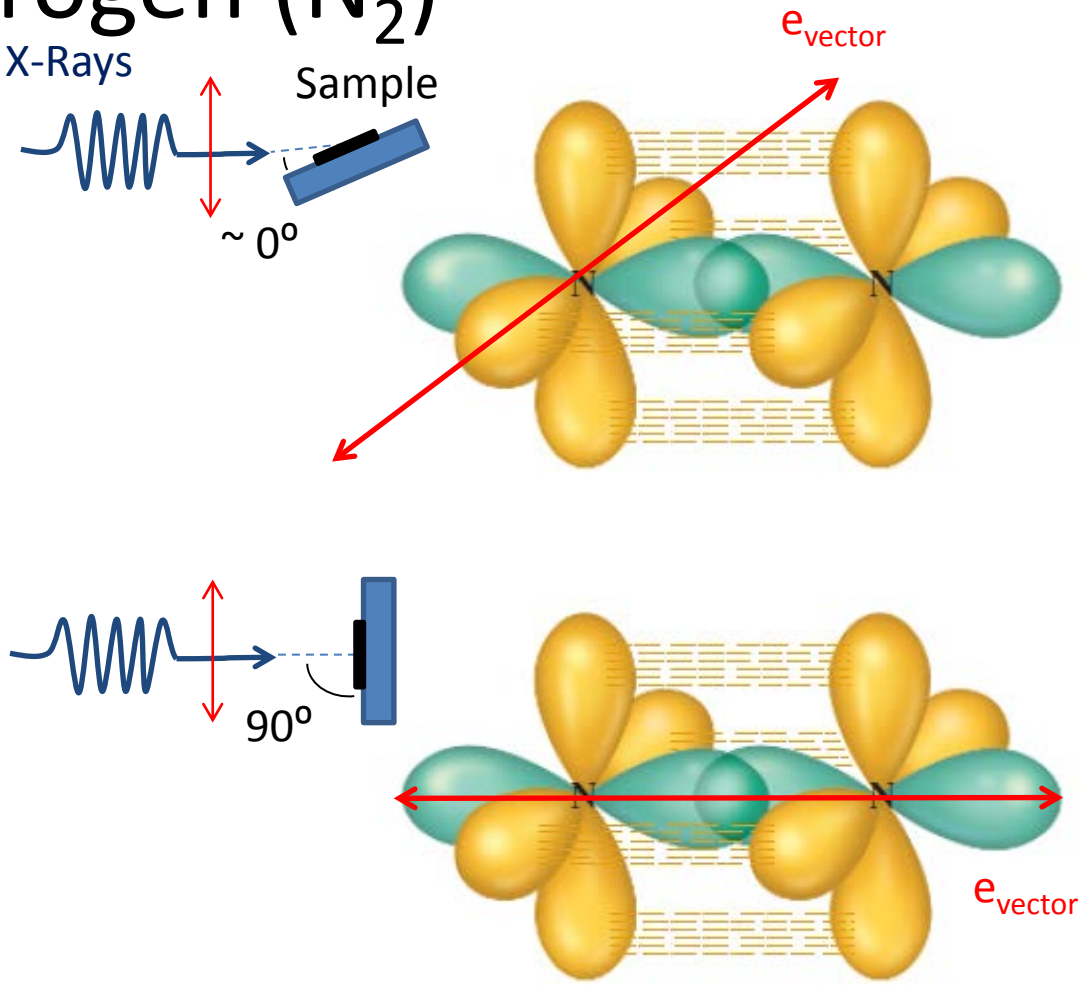
- 1s → 2p gives strongest transitions
- There will be no transition from 1s to s-like orbitals (The integral is zero)
- If orbital has mixed s and p character, only the p-like part of orbital will contribute
- The "dot product" between the e-vector of the incoming light provide sensitivity of spectroscopy to molecular orbital alignment

http://chemwiki.ucdavis.edu/Wikitexts/United_Arab_Emirates_University/UAEU_CHEM_111/Full_Chapters/Full_Chapter_07%3A_Periodic_Properties_of_the_Elements

A Classical Example Using Diatomic Nitrogen (N_2)

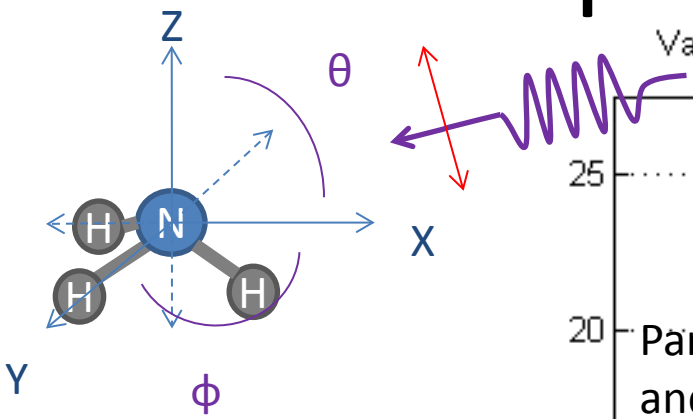


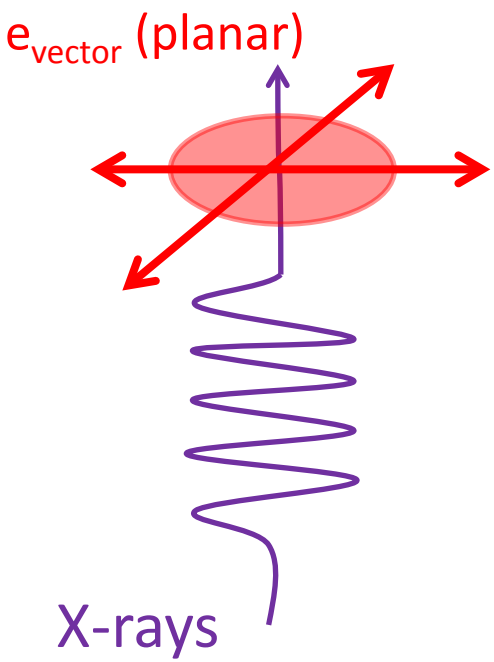
A. Nilsson

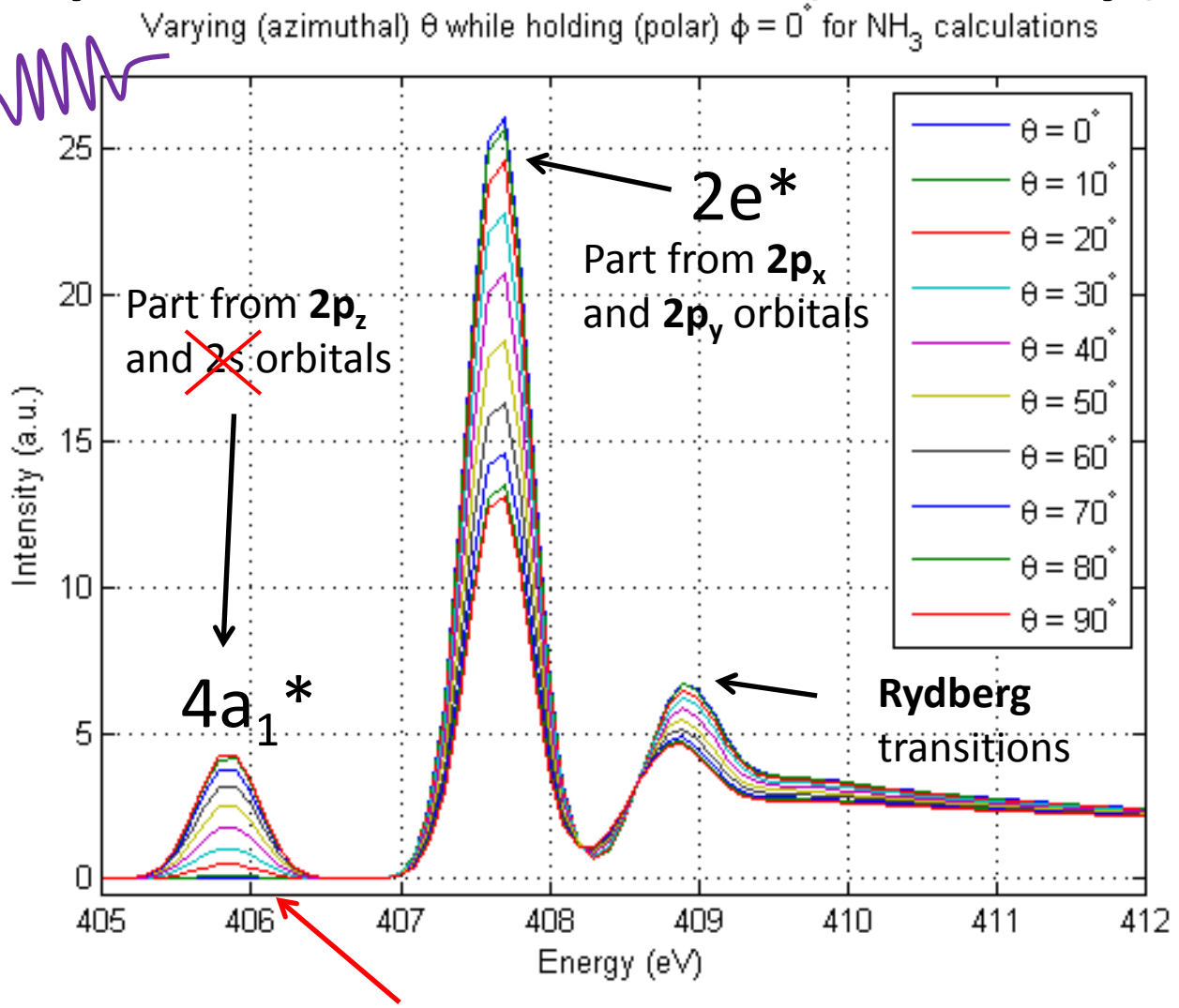


S. S. Zumdahl , S.A. Zumdahl, R. Gomer (editor), Chemistry 8th ed. (Brooks Cole Belmont, 2010) p. 411.

First Principles Calculation (Theory)

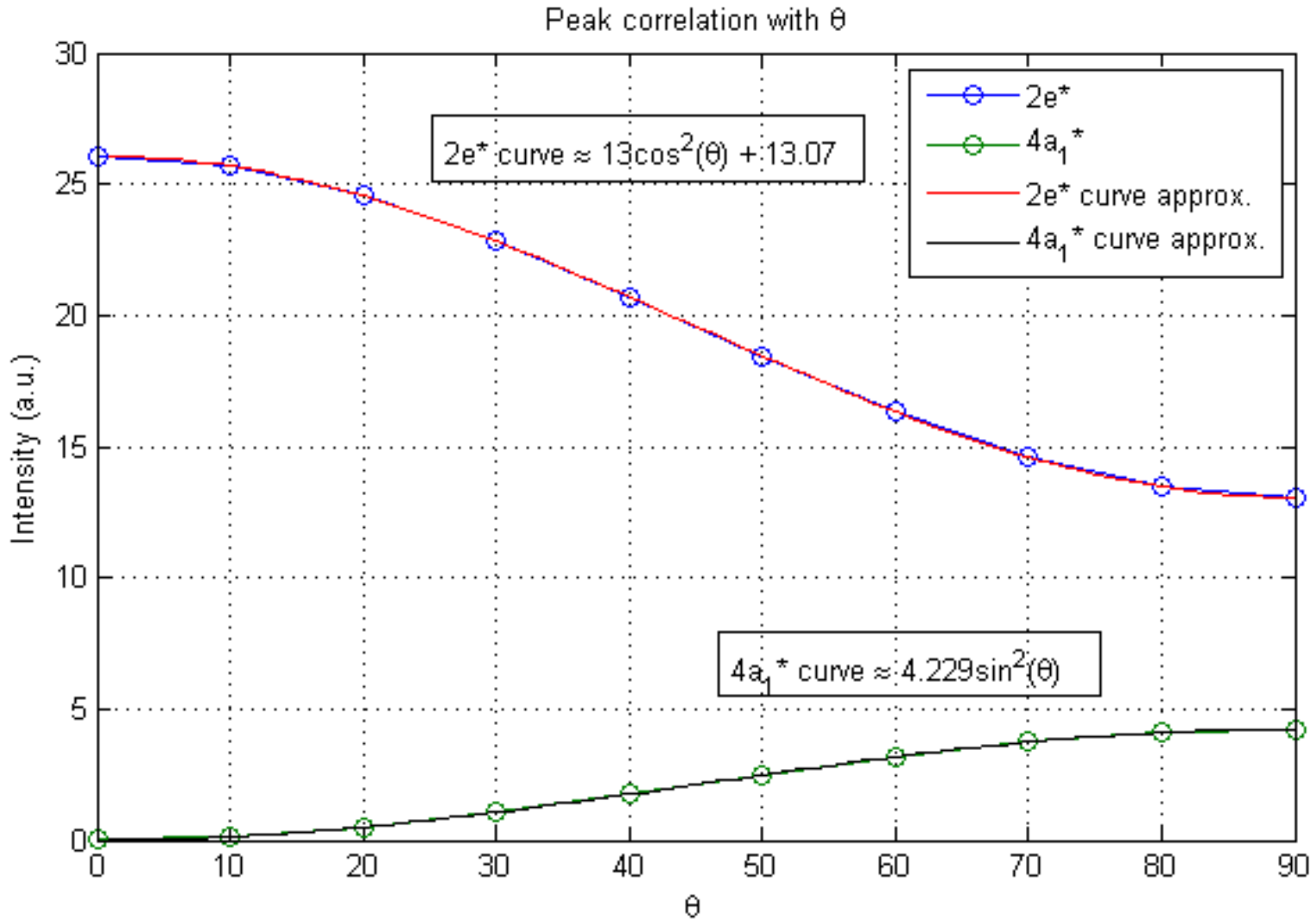






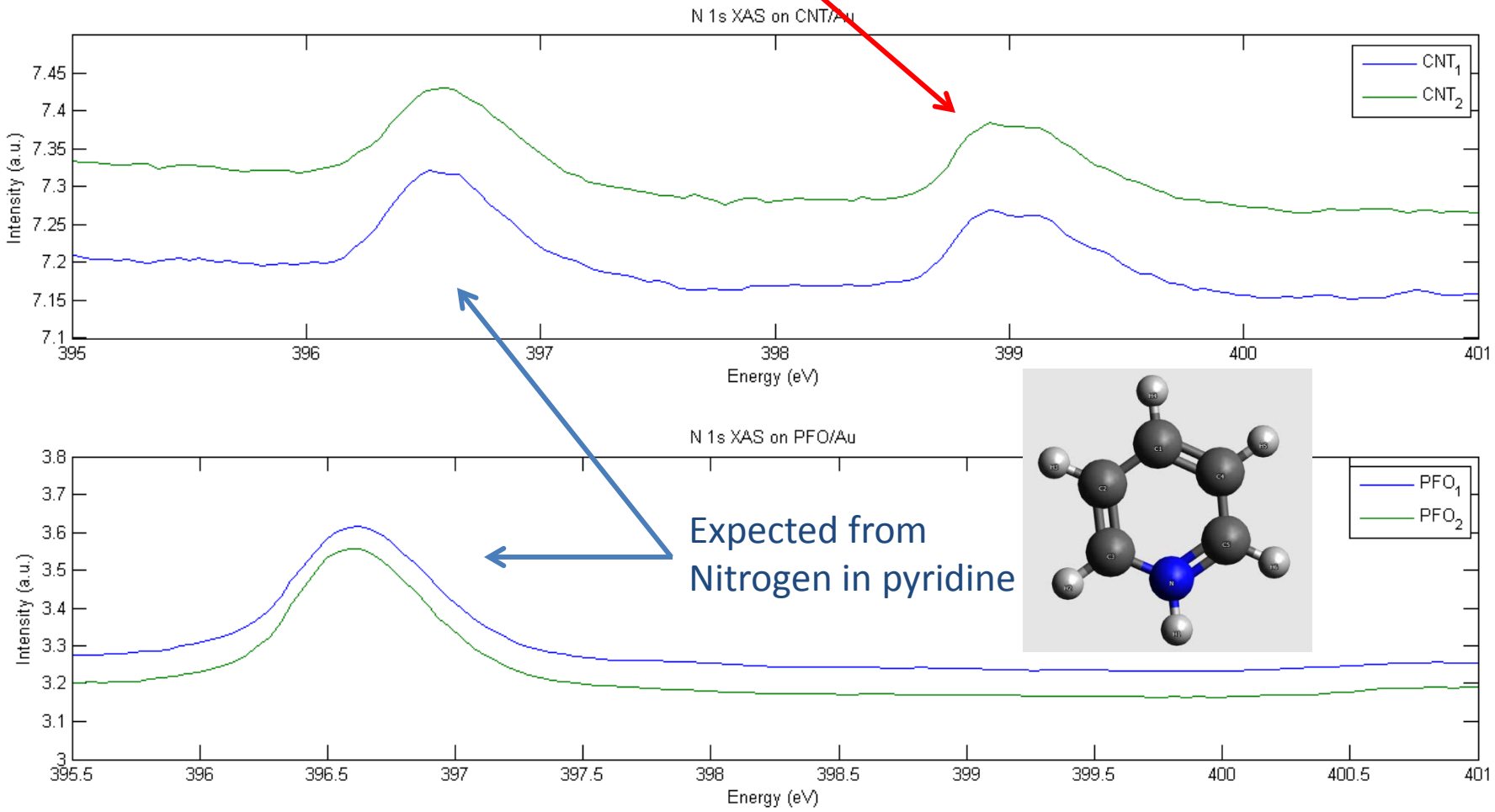
More s character of the Lowest Unoccupied Molecular Orbital (LUMO) decreases the $4a_1^*$ peak (recall the Dipole Selection Rule)

$4a_1$* and 2e* peak correlation with θ

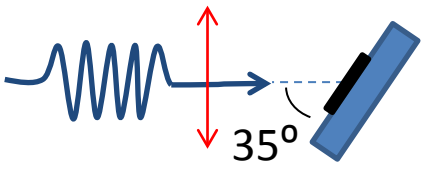


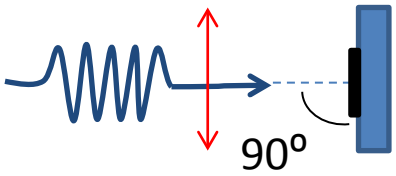
How Will Carbon Nanotubes (CNT) (and Pyridine) Affect Our Data?

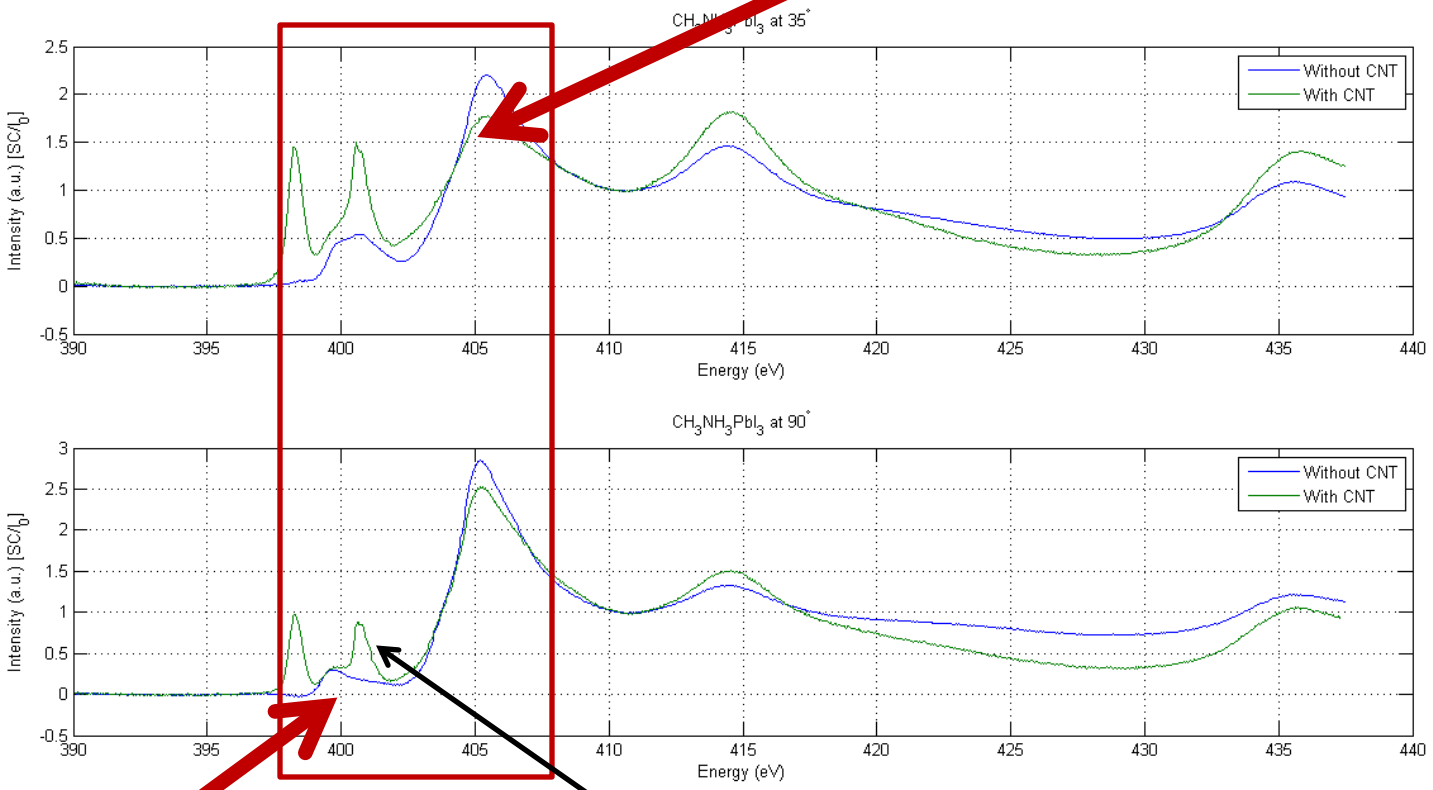
Carbon Nanotubes doped by Nitrogen, Source: Science, 333 (6045), 999 (2011).



N 1s XAS on CNT and Perovskite





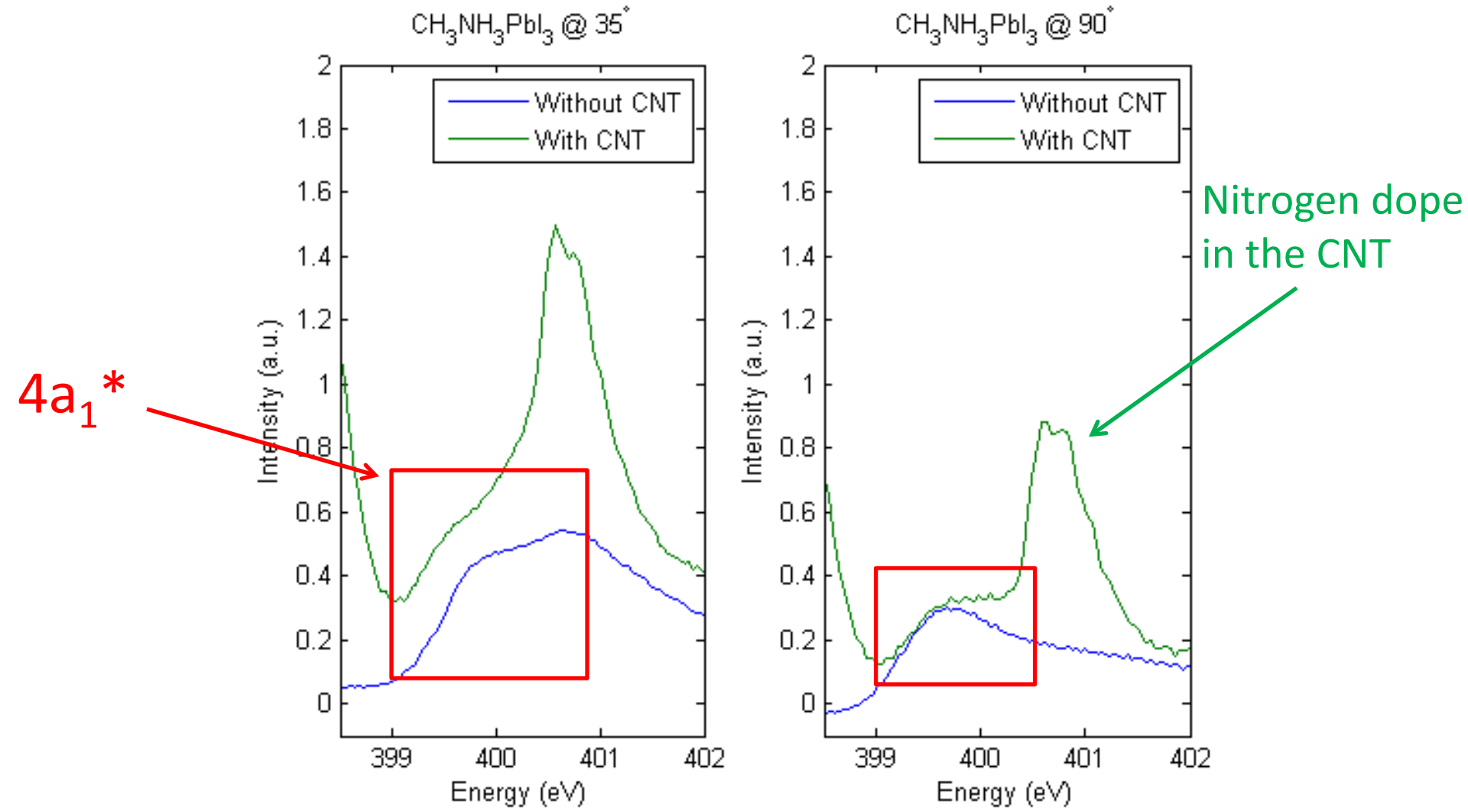


2e* peak decreases

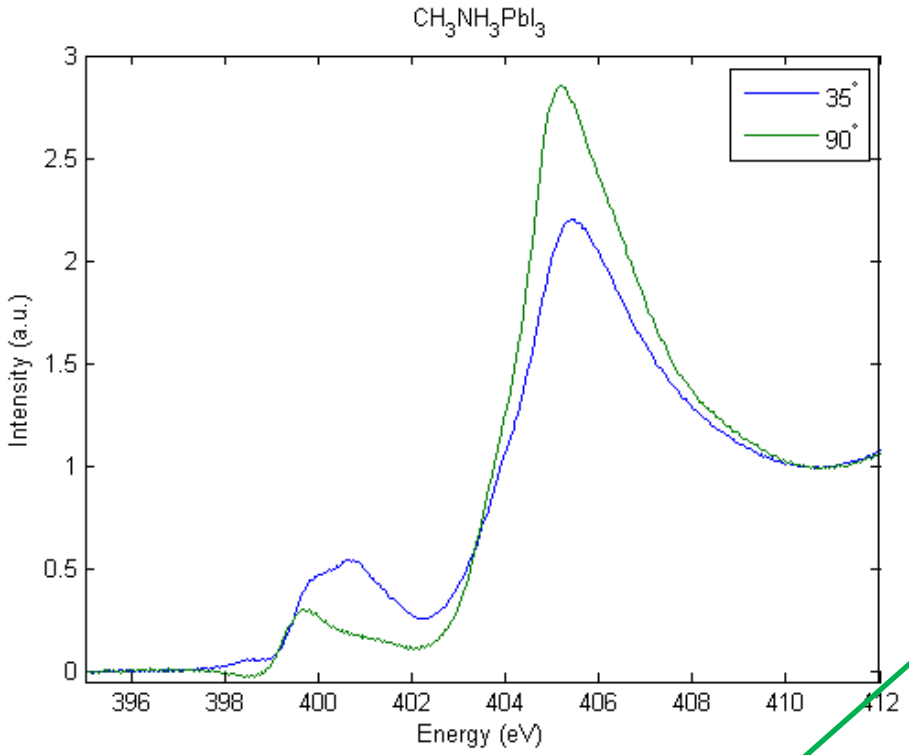
Negligible or small increase to $4a_1$* peak

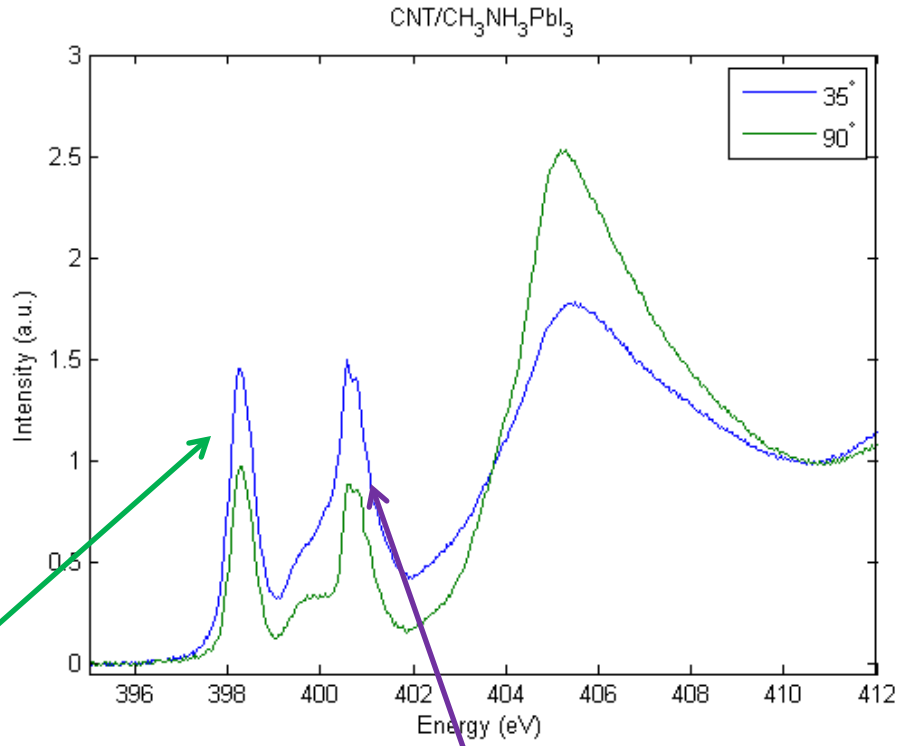
Recall that CNT is doped by Nitrogen causing additional peak, a jump at ~ 401 eV

Concerns About the CNT (Nitrogen doped) Dominating the $4a_1$* Peak



Angular Dependence Preserved With CNT on Perovskite

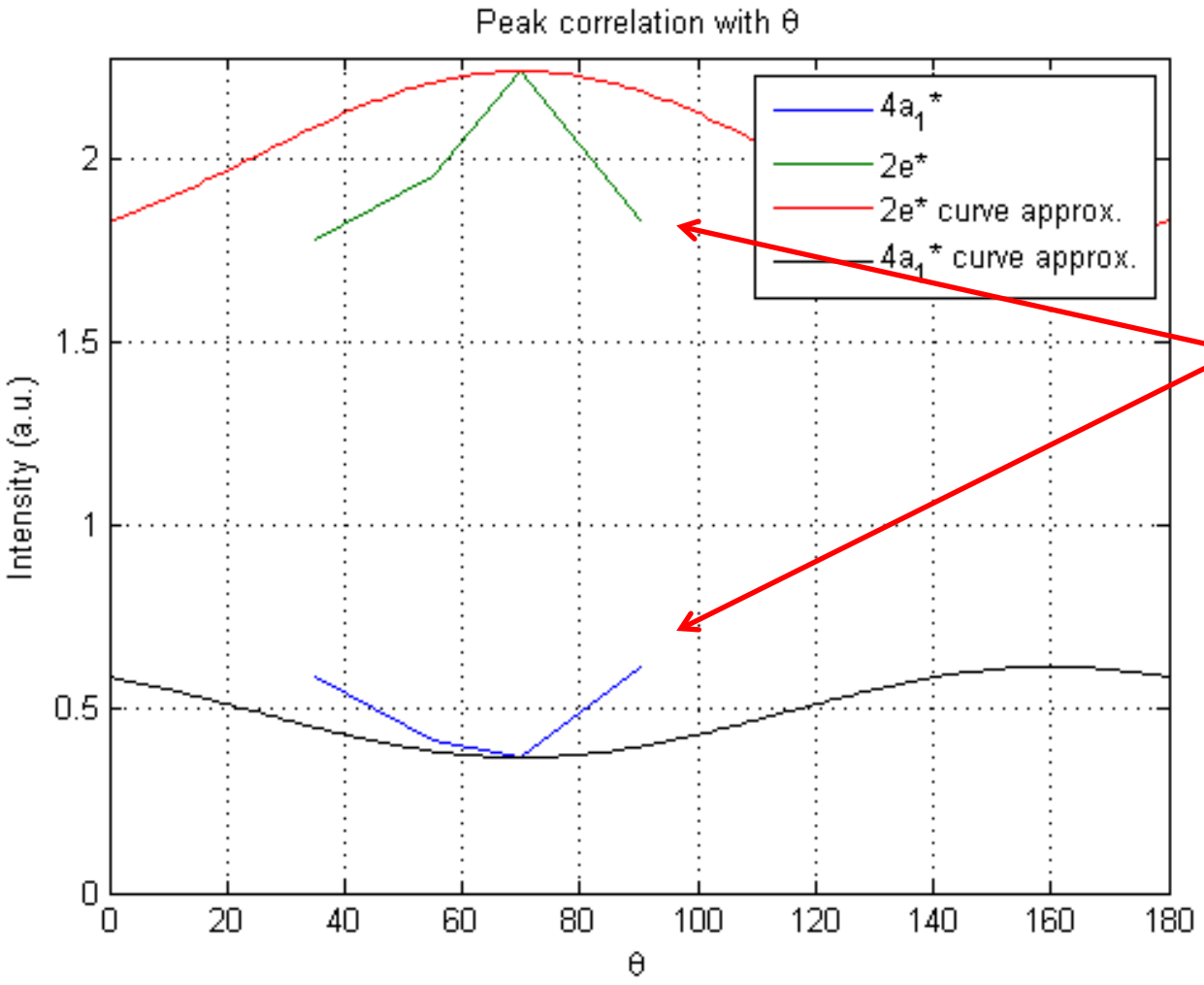




Note that this "extra" peak is from the pyridine in the CNT.

The Nitrogen doping in CNT appears, but $4a_1$* peak is still detectable.

Reason To Repeat Experiment



Good:

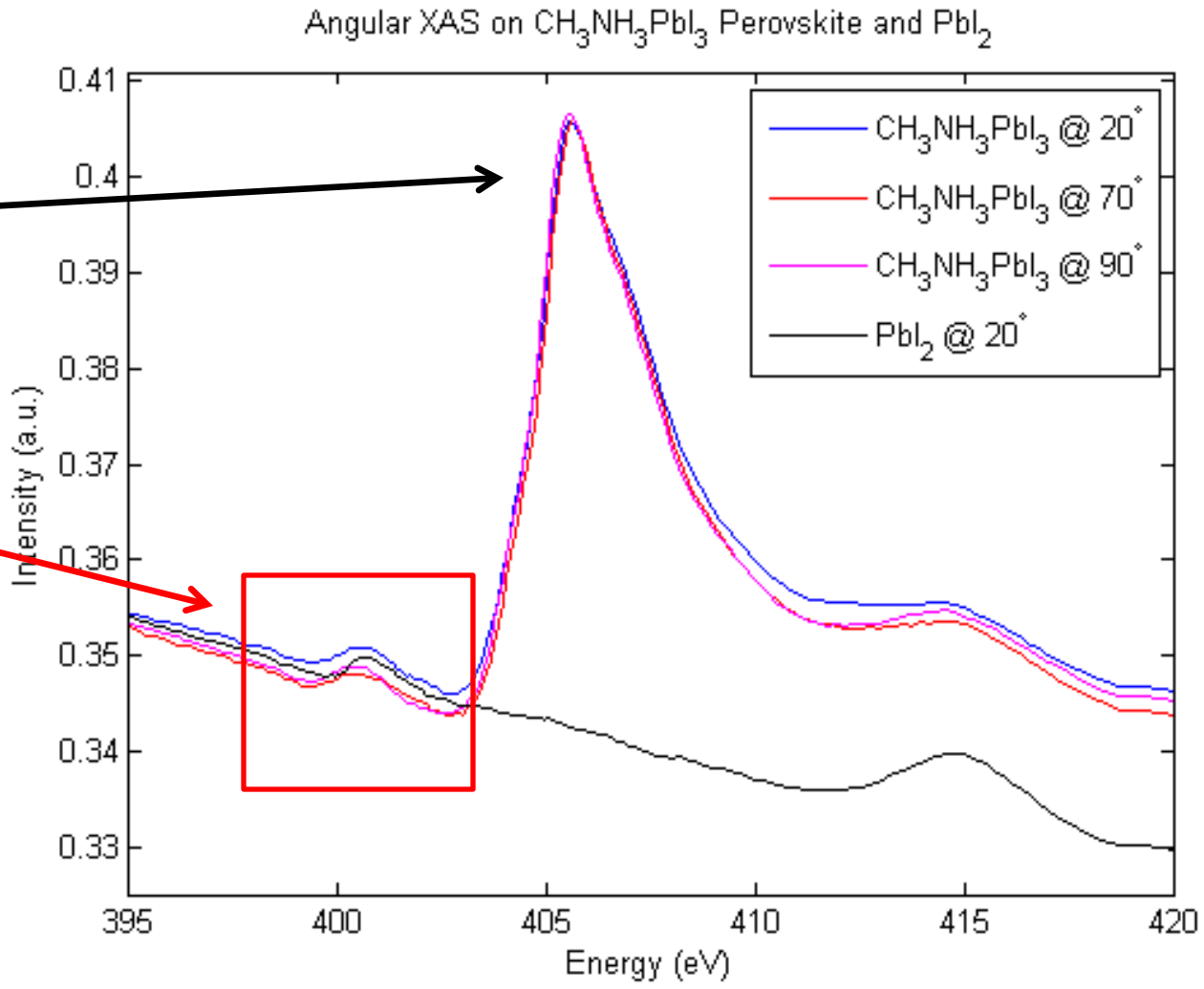
- Relationship between $4a_1$* and 2e* peaks are preserved.

Unexpected:

- Large change between 70 º and 90º scan.
- When rotating polar coordinates, 100º will have same results as 80º (because e-vector is "mostly" planar), but that means $\sin^2(\theta)$ and $\cos^2(\theta)$ curve fitting will not be preserved.
- We wanted to normalize by removing lead (PbI_2)

XAS on Lead and $CH_3NH_3PbI_3$: Concerns & Inconclusive

- No signs of angular dependence in repeat experiment (no CNT).
- Contributions from PbI_2 needs further study (Lead portion of the Perovskite); however, this was detected on the Gold (Au) too, so its a possible contamination.



Next Steps

- We believe there is angular dependence in the CNT/Perovskite film, but we need more data to establish a solid trend.
- We observed angular dependence in one run and none on the other, and we want to know why.
- Contributions from the lead (Pb 4d), pyridine polymer on CNT, and the CNTs alone require careful treatment of data.
- Normalization of data needs to be carefully considered, and contamination carefully avoided for the $4a_1$* region.

Acknowledgement

- This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internship (SULI) program
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- NREL: Philip Schultz, S. Christensen, J. Berry