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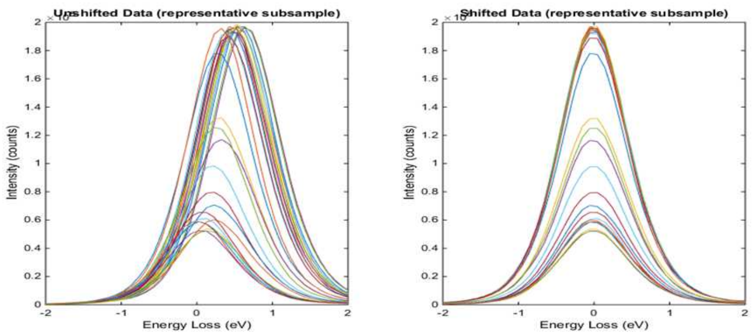

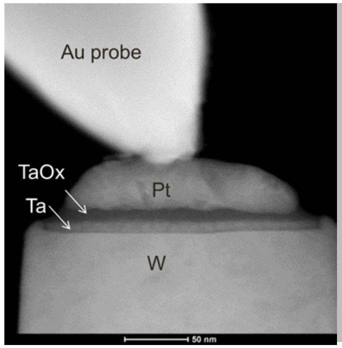

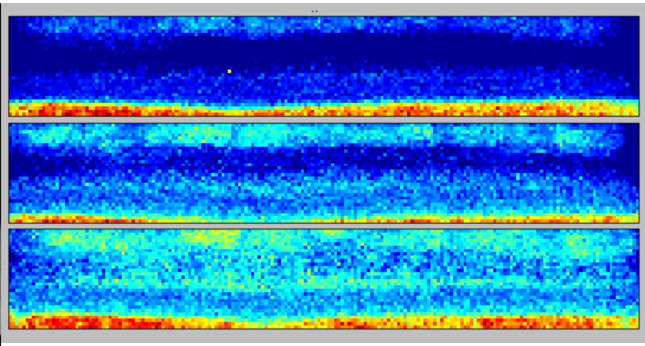

Global Analysis Peak Fitting Applied to EELS Images

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Paper 712, Advanced Analytical TEM/STEM, 2015.08.05 1330

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Overview

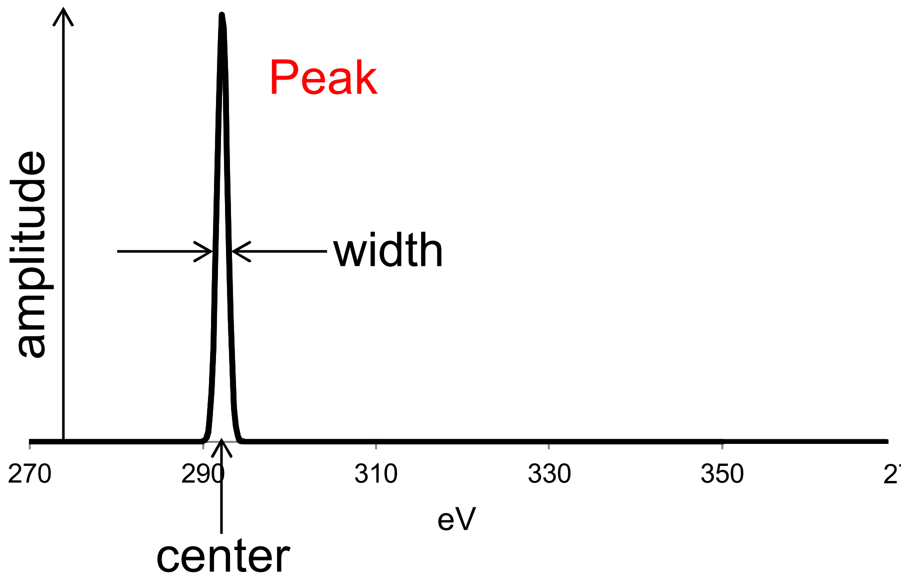
- Curve Fitting and Multivariate Analysis
  - Peak Fitting
  - Least Squares
  - Principal Component Analysis (PCA)
- Previous work on NEXAFS data analysis
  - Analysis of O-ring polymer material
  - Global analysis of NEXAFS images
- Analysis of EELS data
  - Interpretation of spectral images (SI) taken on Pt/TaO_x/Ta stack
  - Multivariate curve resolution (MCR) of EELS images
  - Global analysis of EELS images

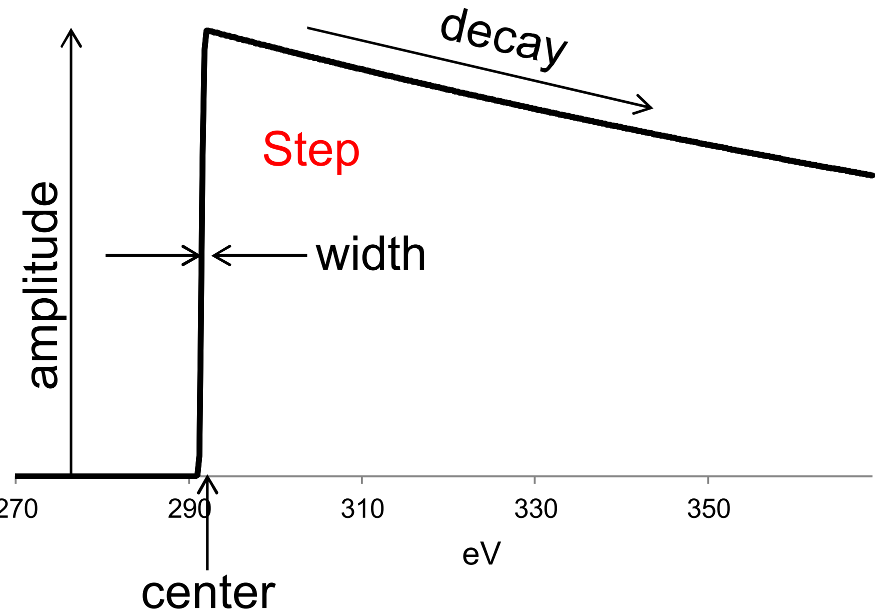
Motivation

- Peak fitting can help elucidate the nature of bonding in polymers
  - Typically, peak fitting is performed on a single spectrum or a summed area in a spectrum image
- Use NEXAFS with global analysis to evaluate ageing mechanisms in polymers
  - Fitting NEXAFS images, multiple spectra simultaneously, can provide information about the areal extent of bonding in the material as well as mixed species
- Understanding behavior of memristor materials using EELS
  - Interpret data using global analysis to understand physical changes in memristors upon electrical challenges

Curve Fitting

- Gaussian and Lorentzian peaks are characterized by three parameters: amplitude, center, and width
- The step function has four parameters: amplitude, center, width, and decay rate





Peak, Step and Offset Definitions

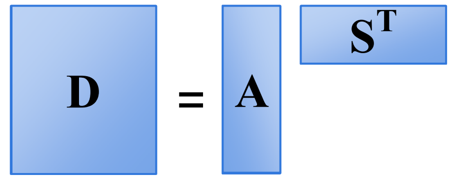
- Gaussian: $I_G = Ae^{-\left(\frac{E-E_0}{w}c\right)^2}$; where $c = 2\sqrt{\log 4}$
- Lorenztian: $I_L = A\left(\frac{\left({}^{w}/_{2}\right)^2}{(E-E_0)^2+\left({}^{w}/_{2}\right)^2}\right)$
- Pseudo-Voigt:

$$I_V = A\left[\eta\left(\frac{\left({}^{w}/_{2}\right)^2}{(E-E_0)^2+\left({}^{w}/_{2}\right)^2}\right) + (1-\eta)e^{-\left(\frac{E-E_0}{w}c\right)^2}\right]$$

- Asymmetric Peaks: Set $w = mE+b$
  - Both m and b are common to all shifted peaks in sample spectra
- Shaped Step: $I_S = A\left[\frac{1}{2} + \frac{1}{2}erf\left(\frac{E-E_0}{w}d\right)\right]$; where $d = 2\sqrt{\log 2}$
  - Can also introduce exponential decay term into step function
- Offset: $I_O = A$
- Red indicates linear term

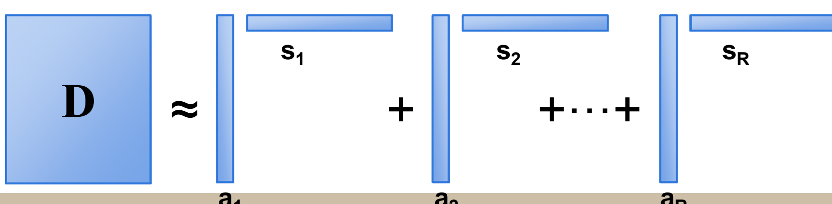
J. Stöhr, *NEXAFS Spectroscopy, Springer, Berlin (1992).*

Set Up the Least Squares Problem



- The model is $\mathbf{D} = \mathbf{A}\mathbf{S}^{\mathrm{T}}$
  - $\mathbf{D}$ is the data matrix, dimensioned as number of image pixels by number of spectral channels
  - $\mathbf{A}$ is the matrix of linear coefficients, dimensioned as number of pixels by number of peaks, steps and offsets (factors)
  - $\mathbf{S}$ is the matrix of nonlinear terms, dimensioned as number of spectral channels by number of factors
  - Superscript T represents matrix transpose
- The least squares criterion: minimize $\left\|\mathbf{D} - \mathbf{A}\mathbf{S}^{\mathrm{T}}\right\|^2$

Least Squares Model



Knorr, F. J. and J. M. Harris, Analytical Chemistry **53(2):** 272-276, (1981).
Beechem, J. M., Numerical Computer Methods. L. Brand and M. L. Johnson, Methods in Enzymology San Diego, Academic Press. **210:** 37-54, (1992).

Solving the Problem

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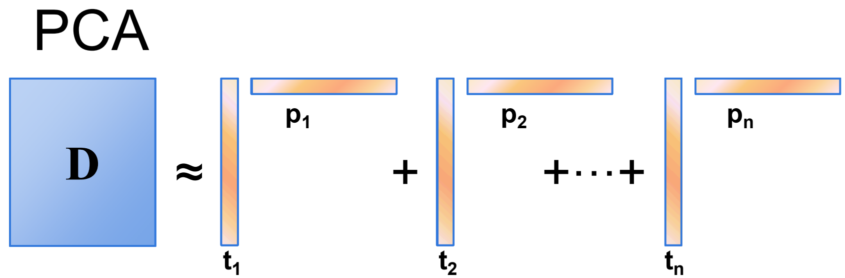
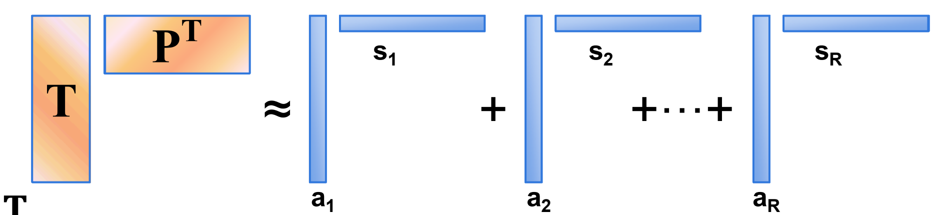
1. Solve nonlinear terms using a nonlinear solver, like nonlinear least squares
   - Initialize with best guesses for peak or step parameters
   - Each peak or step is computed using the estimated parameters and the given energy axis
   - The offset is entered as a column of ones; it has no nonlinear term
2. Given the estimate of $\hat{\mathbf{S}}$ from nonlinear solution, solve the linear terms using least squares
   - $\hat{\mathbf{A}} - \mathbf{D}\hat{\mathbf{S}}\left(\hat{\mathbf{S}}^{\mathbf{T}}\hat{\mathbf{S}}\right)^{-\mathbf{1}}$ (can impose nonnegativity)
   - This is done within the nonlinear function call
3. Iterate until convergence

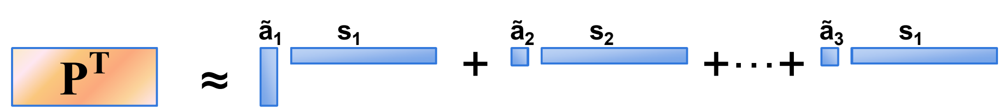
Compression

- We can represent the data as the product of two orthogonal matrices using principal component analysis (PCA): $\mathbf{D} = \mathbf{T}\mathbf{P}^{\mathbf{T}}$



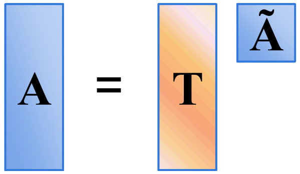
  - $\mathbf{T}$ is the matrix of orthogonal "scores" dimensioned as #pixels by #principal components (#PCs)
  - $\mathbf{P}$ is the matrix of orthonormal "loadings" dimensioned as #spectral channels by #PCs
  - Number of PCs<<min(#pixels,#channels)
- Recall the model is $\mathbf{D} = \mathbf{A}\mathbf{S}^{\mathbf{T}}$
  - Now we can write $\mathbf{T}\mathbf{P}^{\mathbf{T}} = \mathbf{A}\mathbf{S}^{\mathbf{T}}$
  - Finally, we can define $\mathbf{P}^{\mathbf{T}} = \tilde{\mathbf{A}}\mathbf{S}^{\mathbf{T}}$





Compression Use

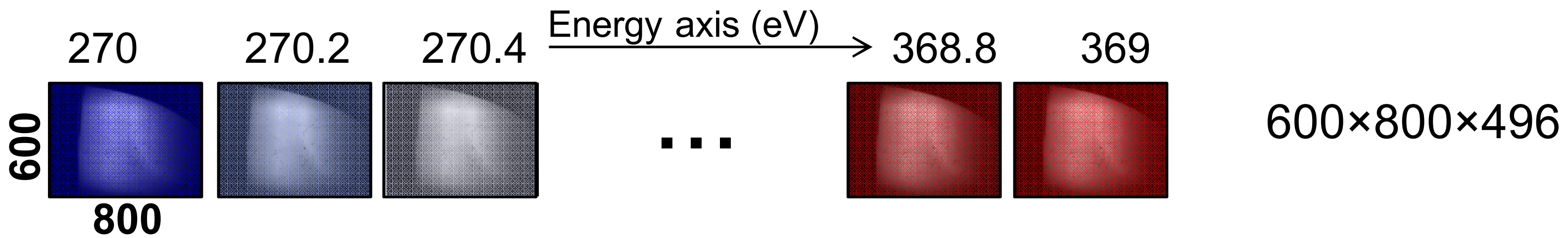
- One can treat the following equation identically to the full data least squares problem
  - Model $\mathbf{P}^{\mathrm{T}} = \widetilde{\mathbf{A}}\mathbf{S}^{\mathrm{T}}$
  - Minimize $\left\|\mathbf{P}^{\mathrm{T}} - \widetilde{\mathbf{A}}\mathbf{S}^{\mathrm{T}}\right\|^{2}$
  - Solve nonlinear part to obtain $\hat{\mathbf{S}}$
  - Solve $\widehat{\widetilde{\mathbf{A}}} - \mathbf{D}\hat{\mathbf{S}}\left(\hat{\mathbf{S}}^{\mathrm{T}}\hat{\mathbf{S}}\right)^{-1}$
  - After convergence compute $\hat{\mathbf{A}} = \mathbf{T}\widehat{\widetilde{\mathbf{A}}}$



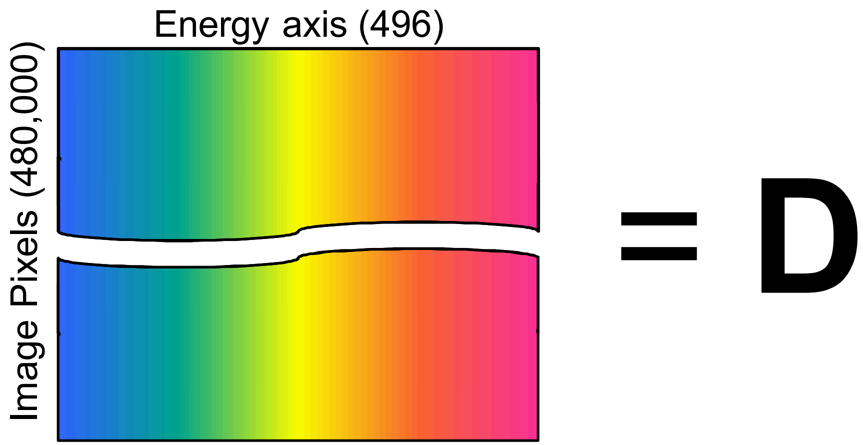
- Nonnegativity can be imposed with only a minor computational penalty

NEXAFS Data Arrays

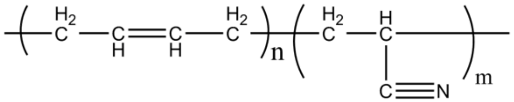
- Consider a collection of Imaging NEXAFS data



- These data can be reorganized as a matrix by stringing out the images as a vector of pixels



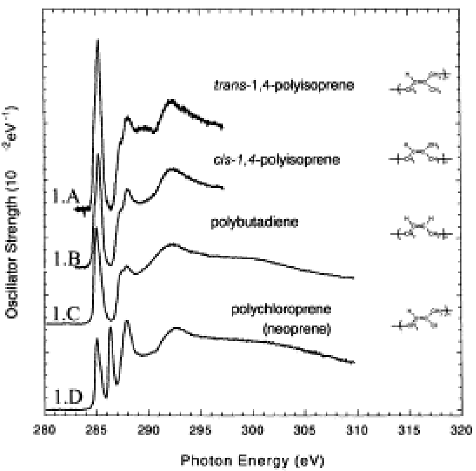
Sample and Analysis Summary

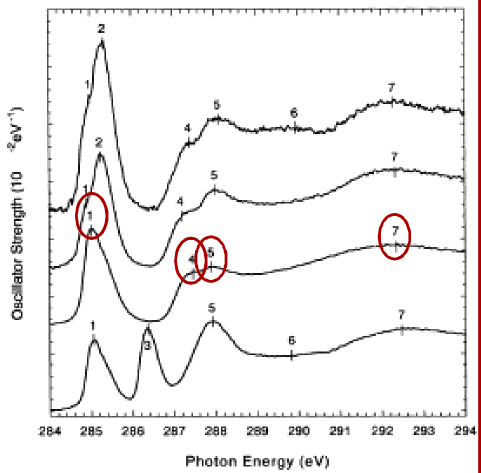


Nitrile Rubber, Buna-N, Butadiene (from www.wikipedia.org)

- KF25 Gasket O-ring, Buna-N, Black--filled with unknown fillers
  - Standard vacuum "quick flange" type commercial O-ring
- O-rings cut into ~1cm length pieces, & artificially aged under different conditions in air ovens
  - Native unaged
  - 125°C, 10 days
  - 125°C, 21 days
- After ageing, ~1mm slices were extracted away from the end of each piece and placed onto sample platen for NEXAFS analysis with double-sided copper tape.
- Analysis Conditions:
  - Samples analyzed on the LARIAT imaging NEXAFS end station located on U7A, National Synchrotron Light Source, BNL.
  - Scanning from 270 to 348eV, 0.2 eV per step (391 spectral channels), 1 second per frame, 2 frames per step, 50V grid bias
- Data file Processing (each individual file):
  - Remove outliers
  - Normalize to I_O
  - Determine variance from duplicate frames
  - Cropped to include only the O-ring material
- 3 Data files concatenated together, then processed with the global analysis routine:
  - 5 symmetrical Voigt peaks, 5 asymmetrical Voigt peaks, 1 step and 1 horizontal offset
  - Constraints for symmetrical Voigt peaks: all have same peak width and must be at a lower energy than the step
  - Constraints for asymmetrical Voigt peaks: must follow model in reference and must be at a higher energy than the step
  - Step location based on similar samples noted in the literature
  - Scale image-mode factor intensities to common total intensity for all samples
  - Images sizes: 47398 pixels + 47349 pixels + 46156 pixels = 140903 pixels x 391 channels

Spectral Peak Assignments





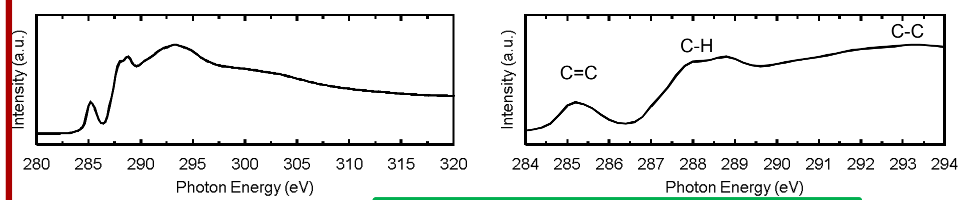
#	Energy (eV) 1.A	1.B	1.C	1.D	Assignment (optical orbital) C-H	C-C	C-Cl
1	284.85	284.85	285.14	285.11	$1\pi^*_{C=C}$		
2	285.28	285.28				$1\pi^*_{C=C}$	
3				286.37			$1\pi^*_{C=C}$
4	287.18	287.15	287.27		σ^*_{C-H}		
5	288.66	288.01	288.01	287.91	σ^*_{C-H}		
6	289.7			289.9			
7	292.3	292.8	292.5	293.3		σ^*_{C-C}	

(1.A) *trans*-1,4-polyisoprene, (1.B) *cis*-1,4-polyisoprene, (1.C) polybutadiene, (1.D) polychloropren

Fig. 3 (a) C 1s N_{EXAFS} spectra of trans -1,4-polyisoprene (1.A), cis -1,4-polyisoprene (1.B), mixed isomer polybutadiene (1.C), and mixed isomers polychloroprene (Neoprene) (1.D). (b) Expanded low energy region of the sam...

O. Dhez, H. Ade, and S. G. Urquhart, **Calibrated NEXAFS Spectra of Some Common Polymers**, *Journal of Electron Spectroscopy and Related Phenomena, 128 (2003), 85-96.* http://dx.doi.org/10.1016/S0368-2048(02)00237-2

Mean O-ring NEXAFS spectrum in this work



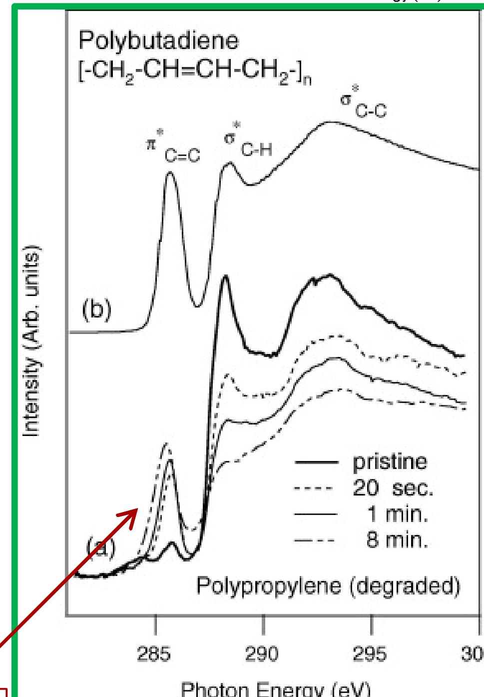
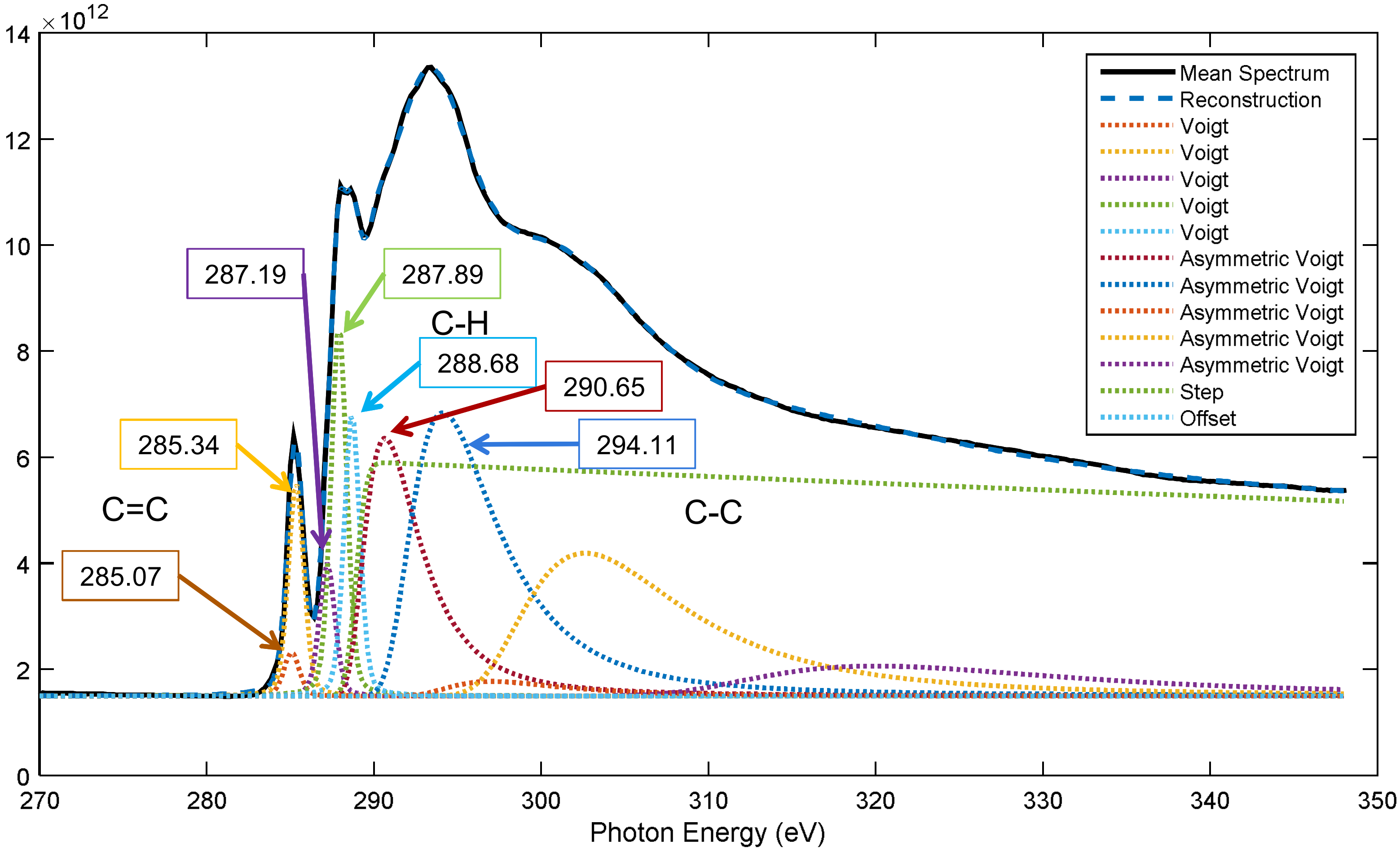


Fig. 5 (a) A series of carbon K-edge NEXAFS spectra of pristine and degraded polypropylene thin-films with different photon-irradiation time. (b) NEXAFS spectrum of polybutadiene polymer.

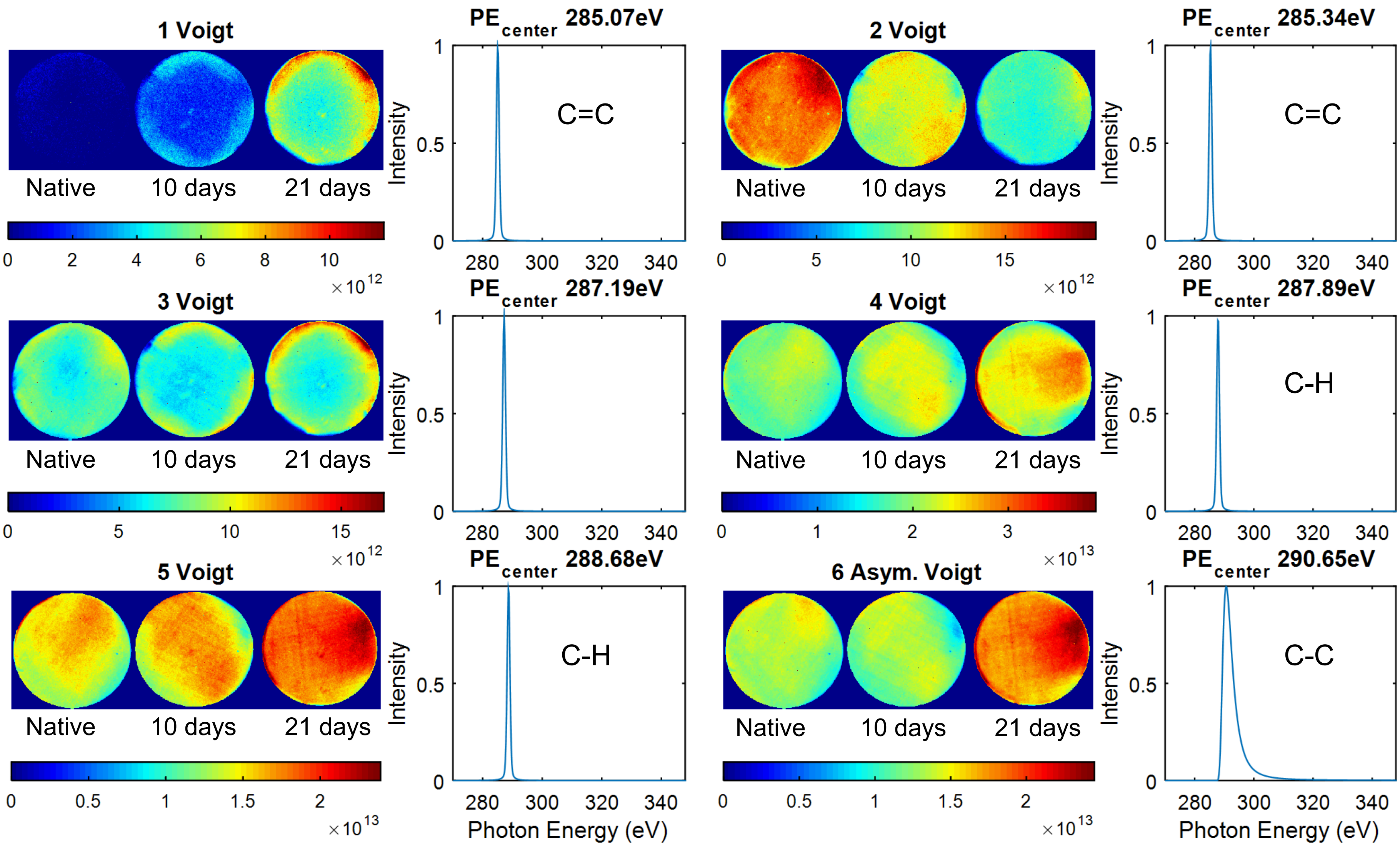
P. H. Zhou, O. Kizilkaya, and E. Morikawa, **Electronic Structure of Photo-Degraded Polypropylene Ultrathin Films**, *Chemical Physics Letters, 465 (2008), 241-44.* http://dx.doi.org/10.1016/j.cplett.2008.10.006

C=C bond formation upon degradation with 80eV photons

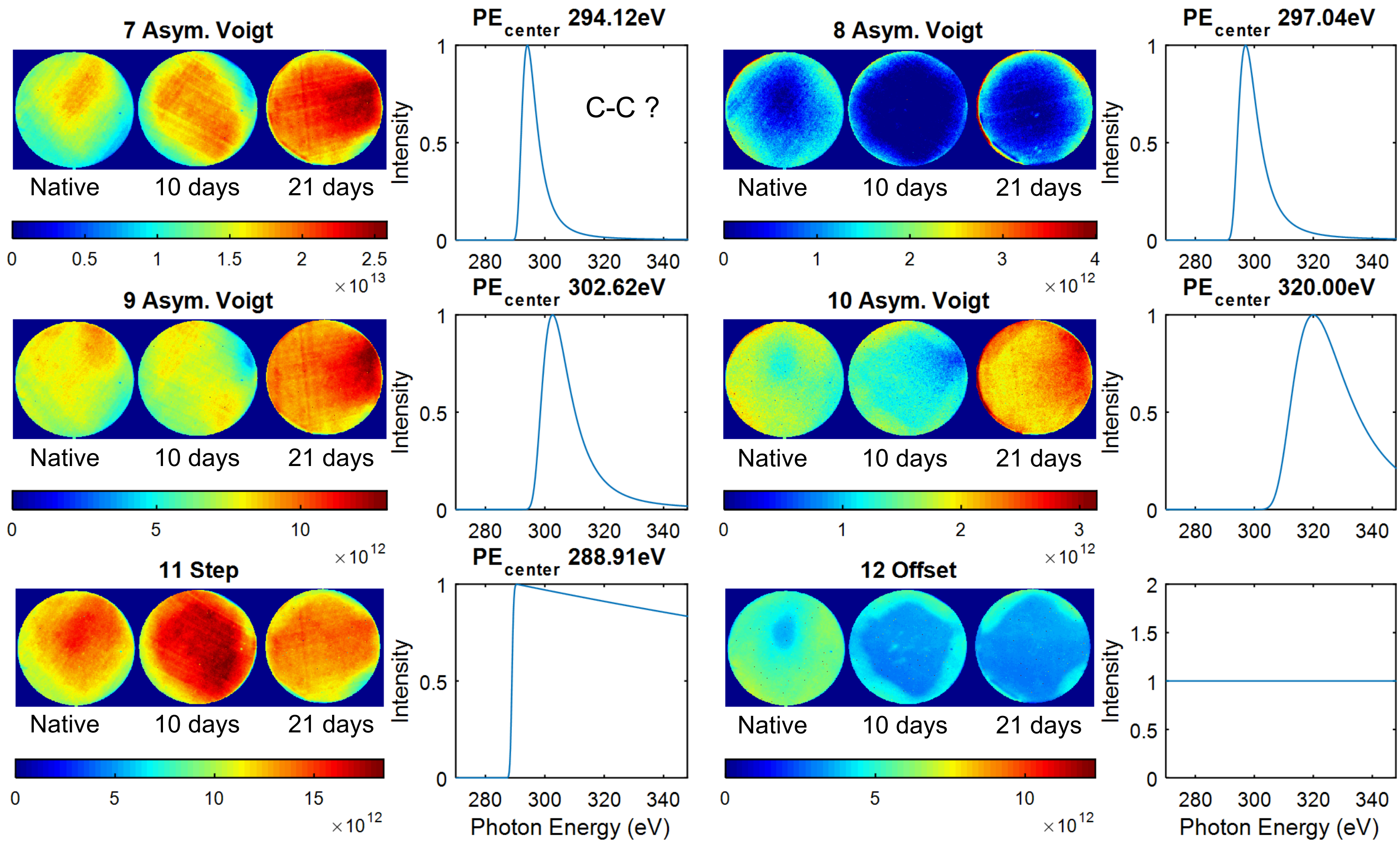
Total Spectrum Fit



Global Analysis Factors 1-6



Global Analysis Factors 7-12



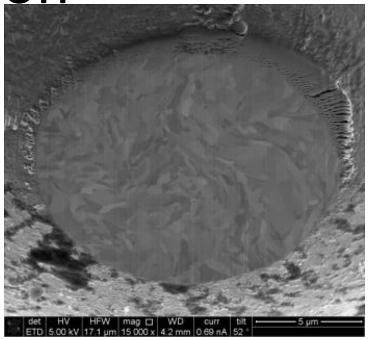
NEXAFS Results

- Used NEXAFS acquired data to analyze aged O-ring material
  - Used peak fitting to insinuate an explanation for ageing details
  - Model suggests ageing influences on C=C bond energies
- Developed and implemented a fast multivariate method of peak fitting for NEXAFS data
- Capable of fitting many spectra simultaneously
  - Currently used to fit single images
  - Could be applied to multiple images or spectra
- Method takes advantage of image inhomogeneities during fitting process
  - Shows promise for finding variation in the spatial domain to aid in data interpretation

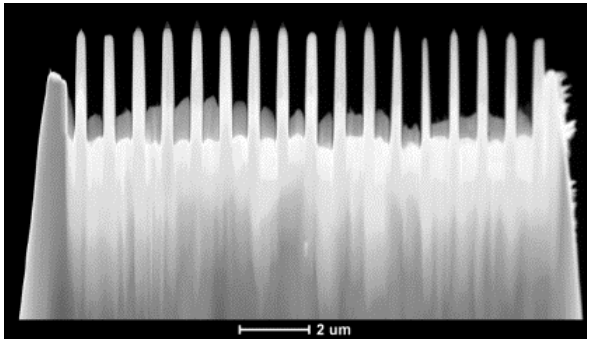
EELS Sample Prep and Acquisition

- Sample preparation
  - Tungsten wire tip

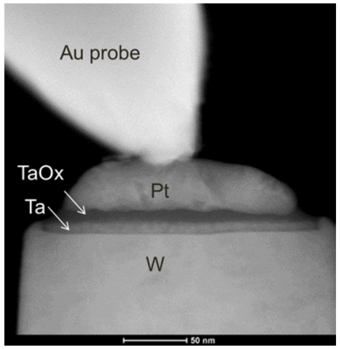
  Flat-topped to ~10µm



  - Sputter deposit Pt/TaOx/Ta stack on W tip
  - Mill comb structure into the surface
    - Electrically isolates the structures
    - 100-200 nm wide, 30-40 nm in beam direction



  - Challenge stack with probe



- EELS Images
  - Collect before, during and after challenge.
- FEI Titan G2 80-200 TEM/STEM
  - 200 kV
  - High-brightness Schottky field emission electron source
  - Spherical aberration corrector on probe forming optics (AC-STEM)
  - Gatan Quantum 963 EELS.
- STEM acquired full EELS spectral images (SI)
  - Low-loss energy region (-20 eV-180 eV)
  - Includes zero-loss peak, plasmons and Ta $O_{2,3}$ edge, with a 50 msec dwell time
  - Data size: 30 x 190 pixels x 550 channels x 3 states

EELS-SI data preprocessing

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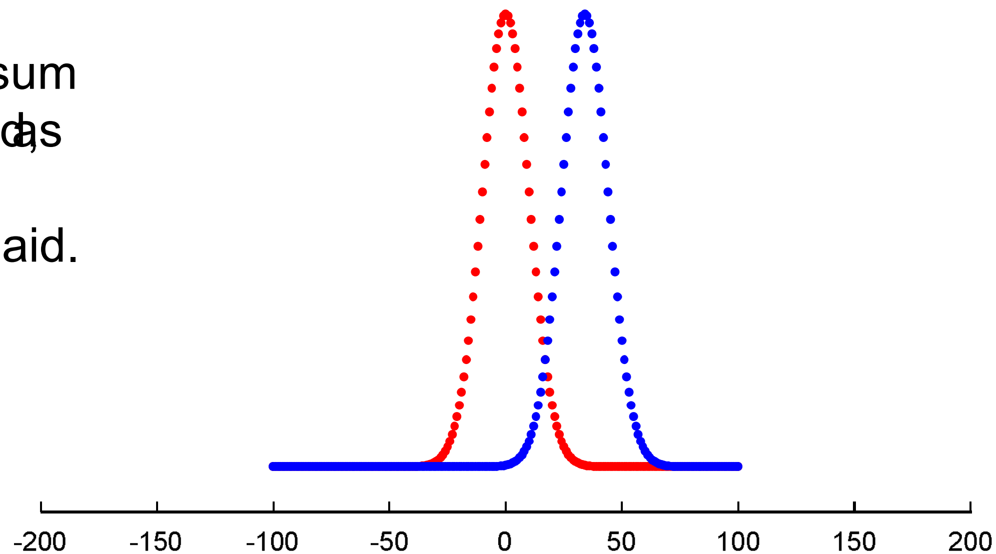
- Energy Axis Alignment
  - Correcting for small instabilities in the primary beam energy and drift/instability of power supplies.
- Use the region of the zero loss peaks
  - Restrict data set to -3 eV to +3 eV
  - Upsampled data by fifty times
    - Effective channel size of 2 meV
  - Used Piecewise Cubic Hermite Interpolating Polynomial (PCHIP)
  - Computed the cross-correlation coefficients across the zero loss peaks
    - Align each pixel spectrum relative to the first row, first column pixel of the before-challenge sample
    - Choosing the index of the maximum cross-correlation coefficient as the zero loss value
    - Shifts all the spectral to a common energy-loss baseline

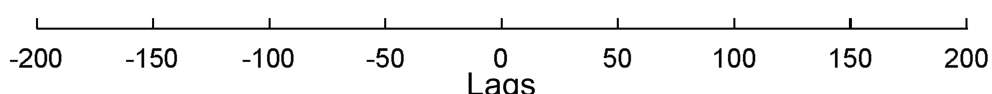
Peak Alignment Cross-Correlation

Consider two identical, but shifted, Gaussian curves.

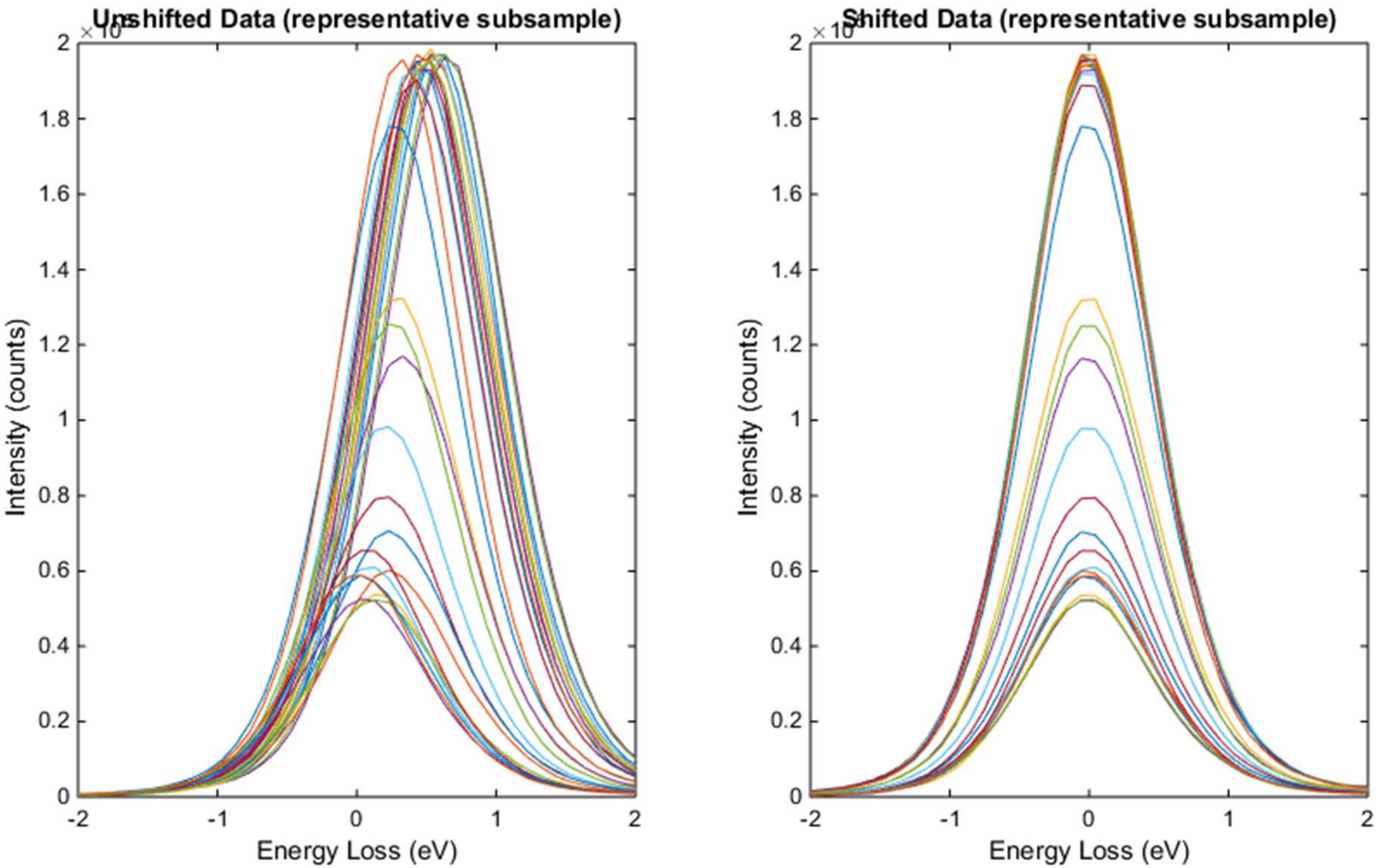
Compute product-sum for each increment as the curves are progressively overlaid.



Determine the lag at the value of the maximum cross-correlation.

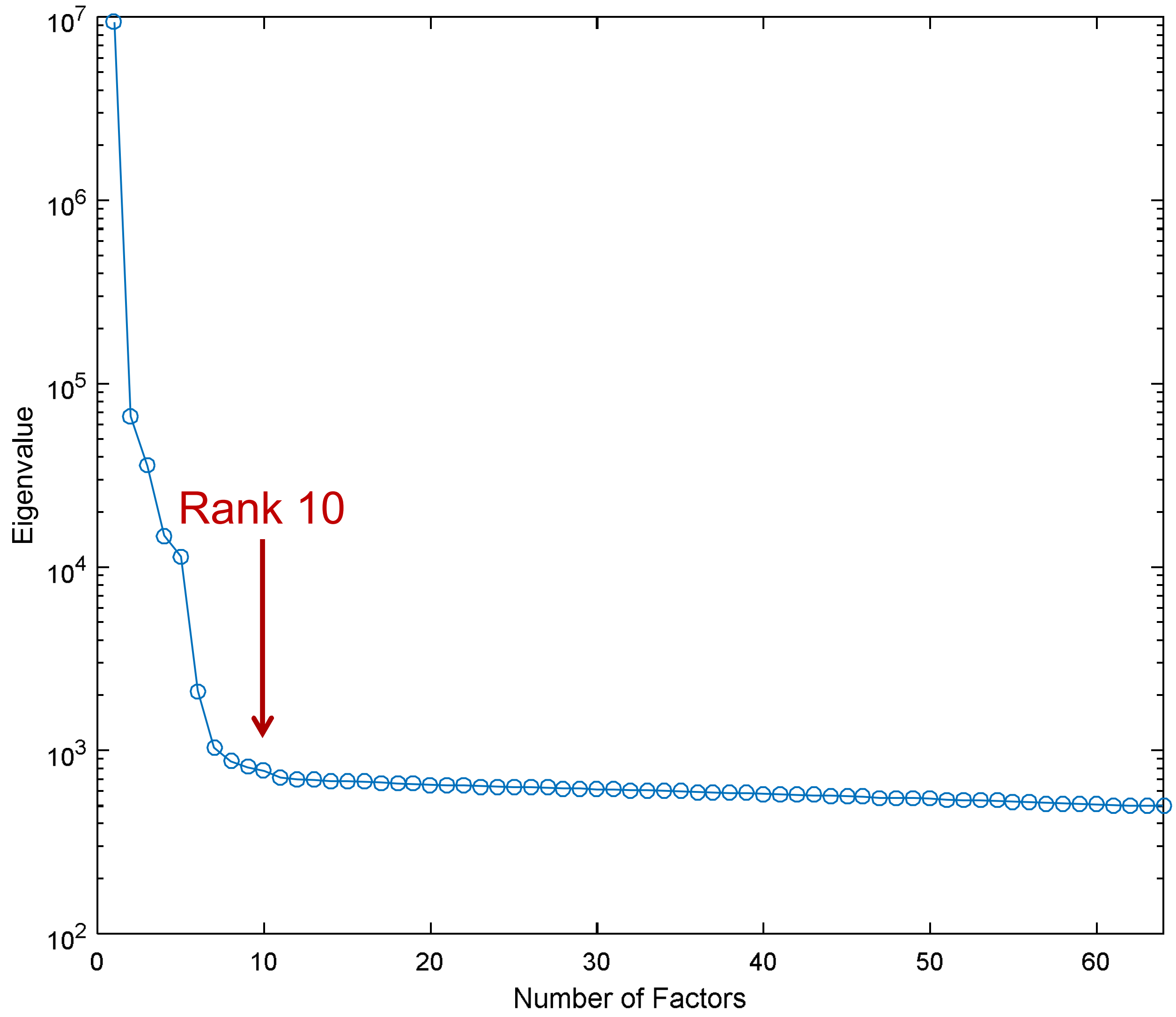


Effects of Alignment Procedure

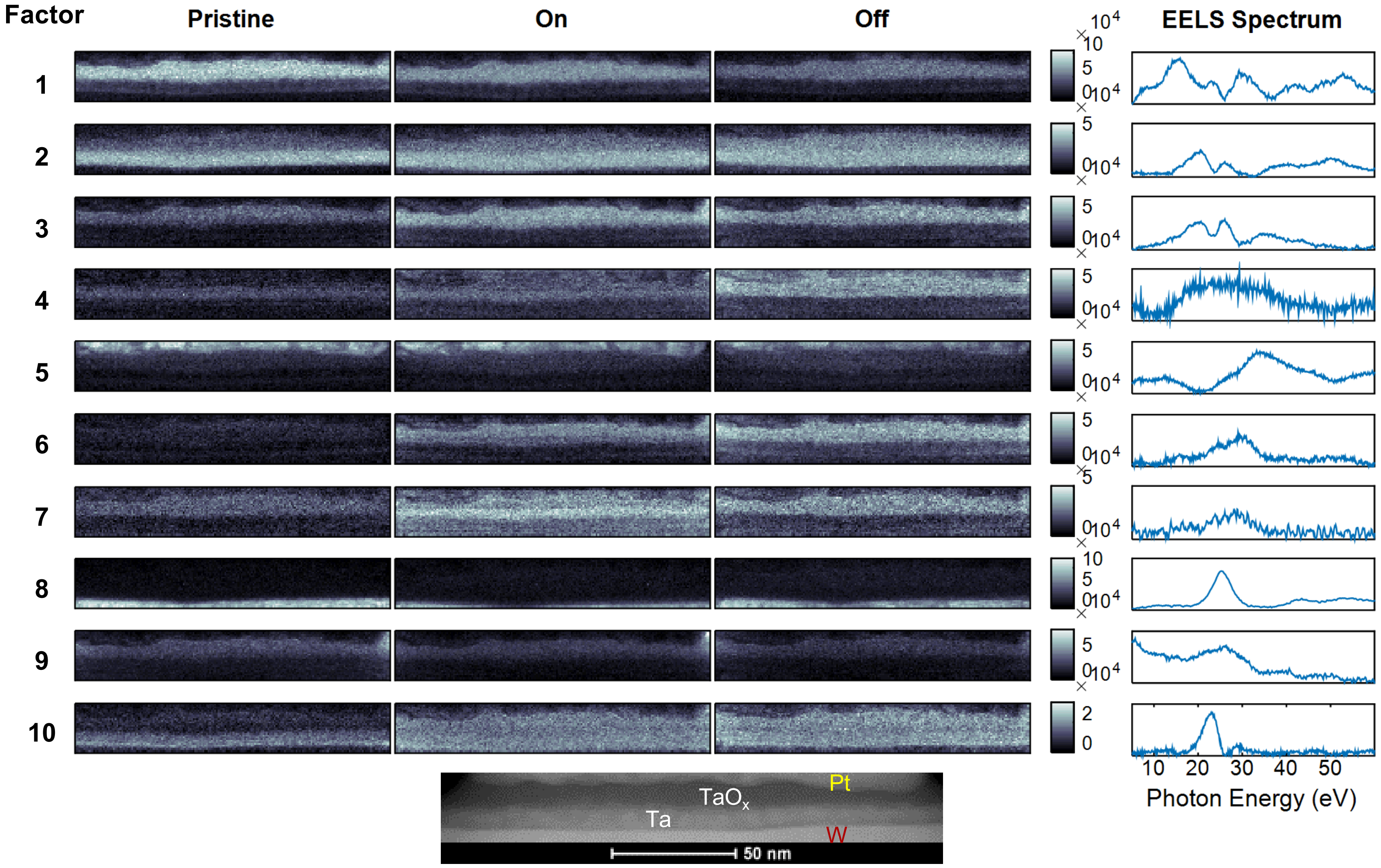


Alignment of EELS-SI zero loss peaks

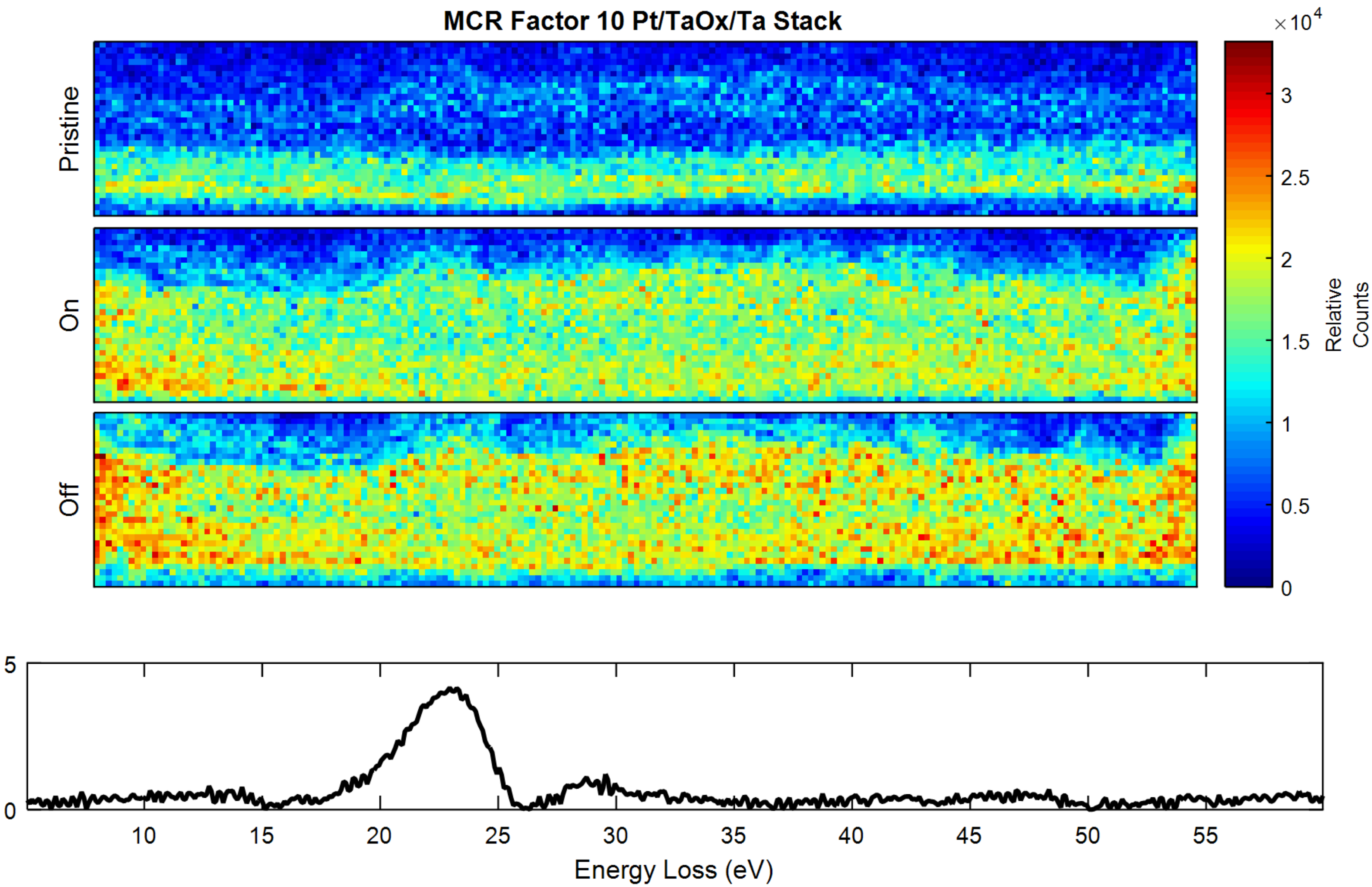
Eigenanalysis of Combined, Shifted Data



MCR Factor Analysis Results

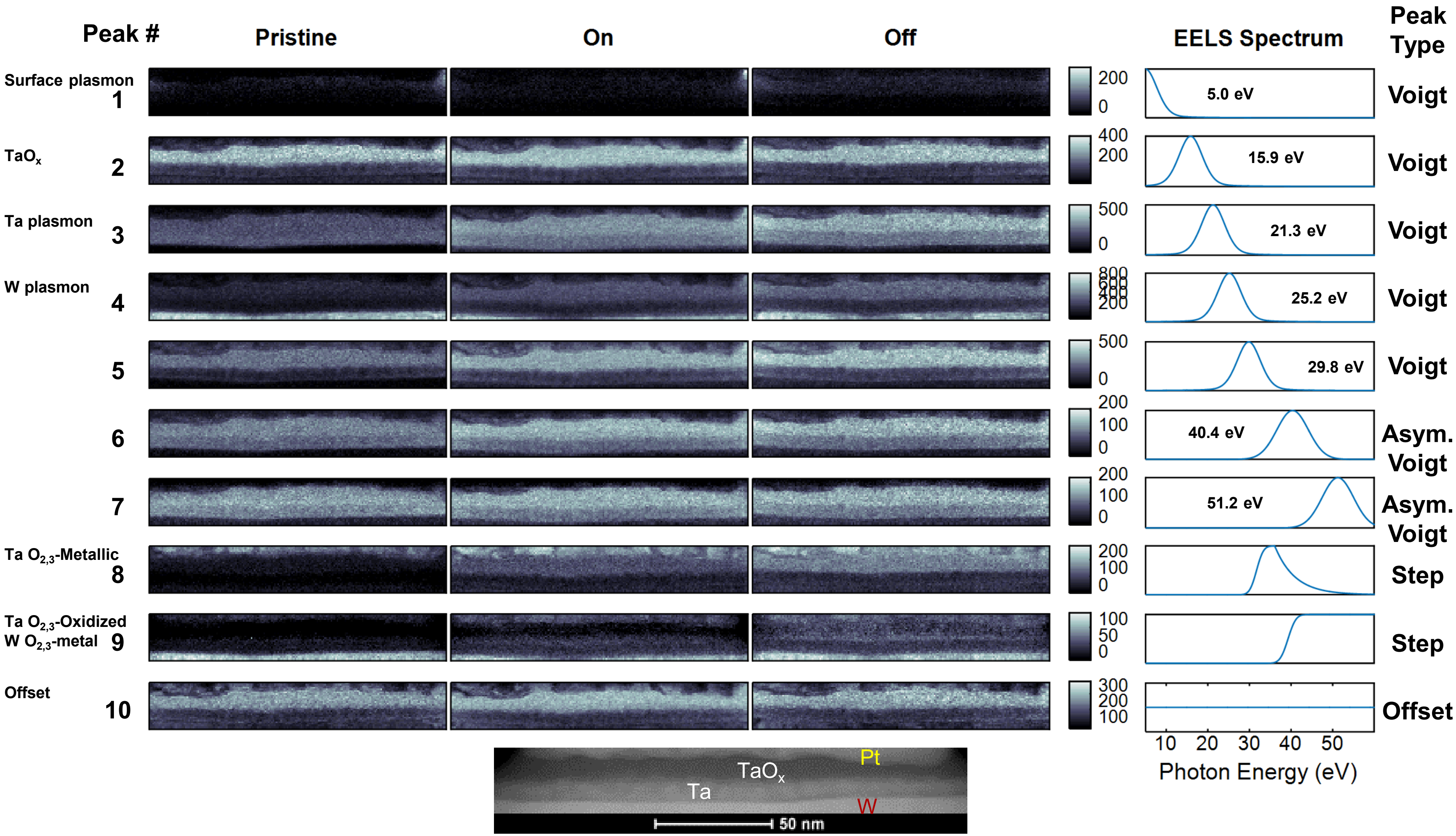


MCR Factor 10

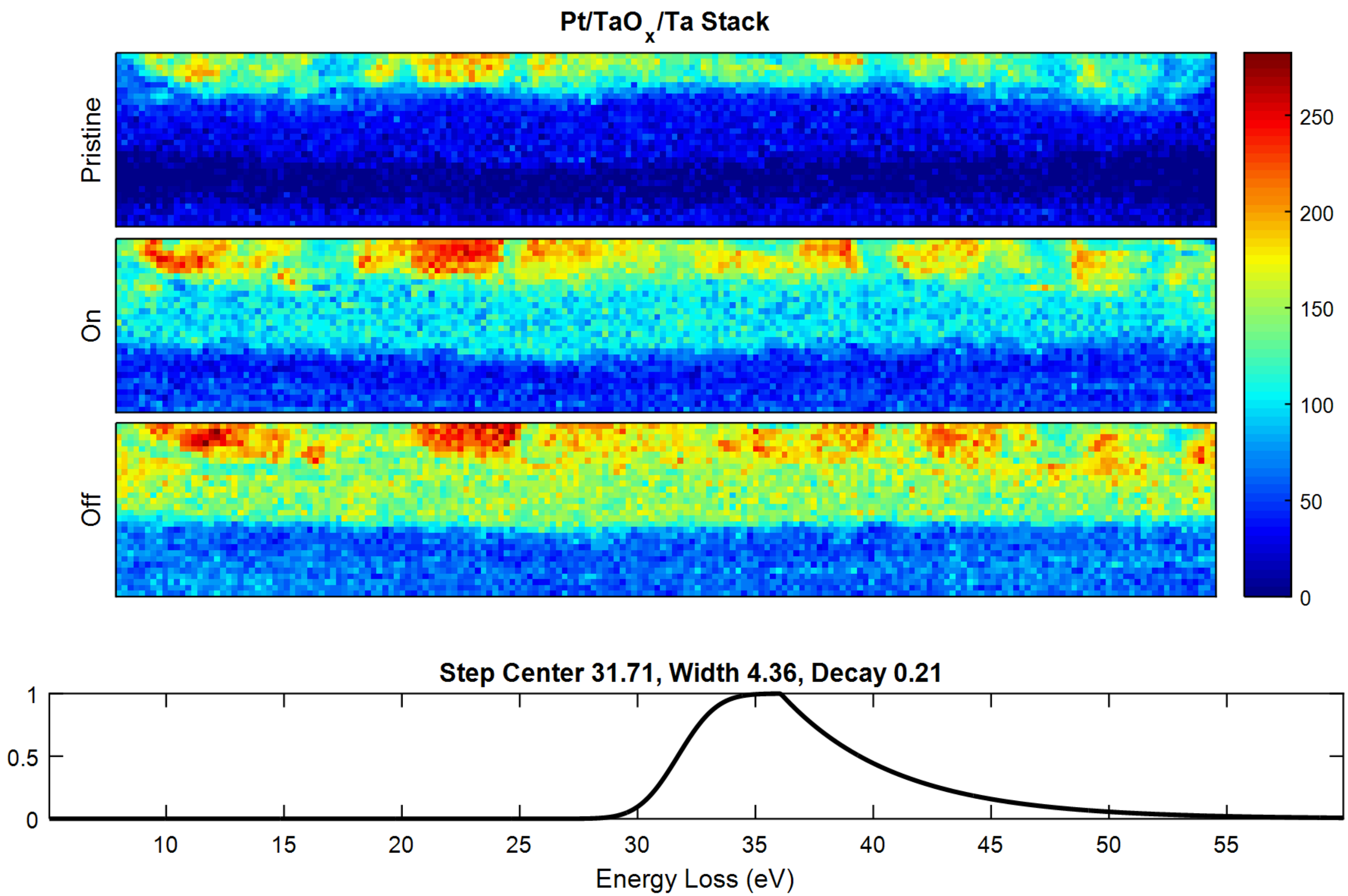


No evidence of conductor filaments or channels in the TaO_x region, although this factor shows a noticeable affect from the challenge

Global Analysis Results

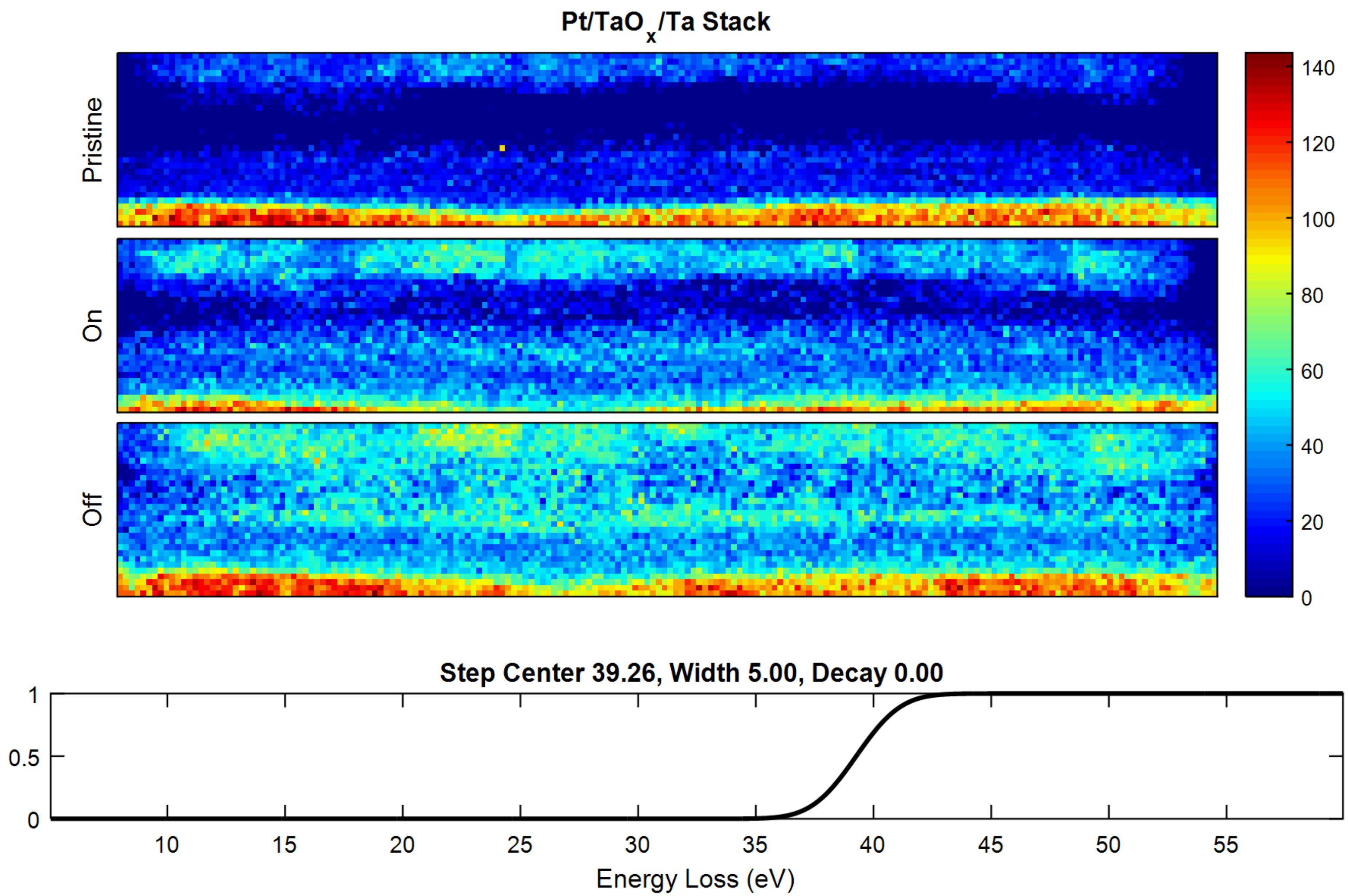


Ta $O_{2,3}$-Metallic



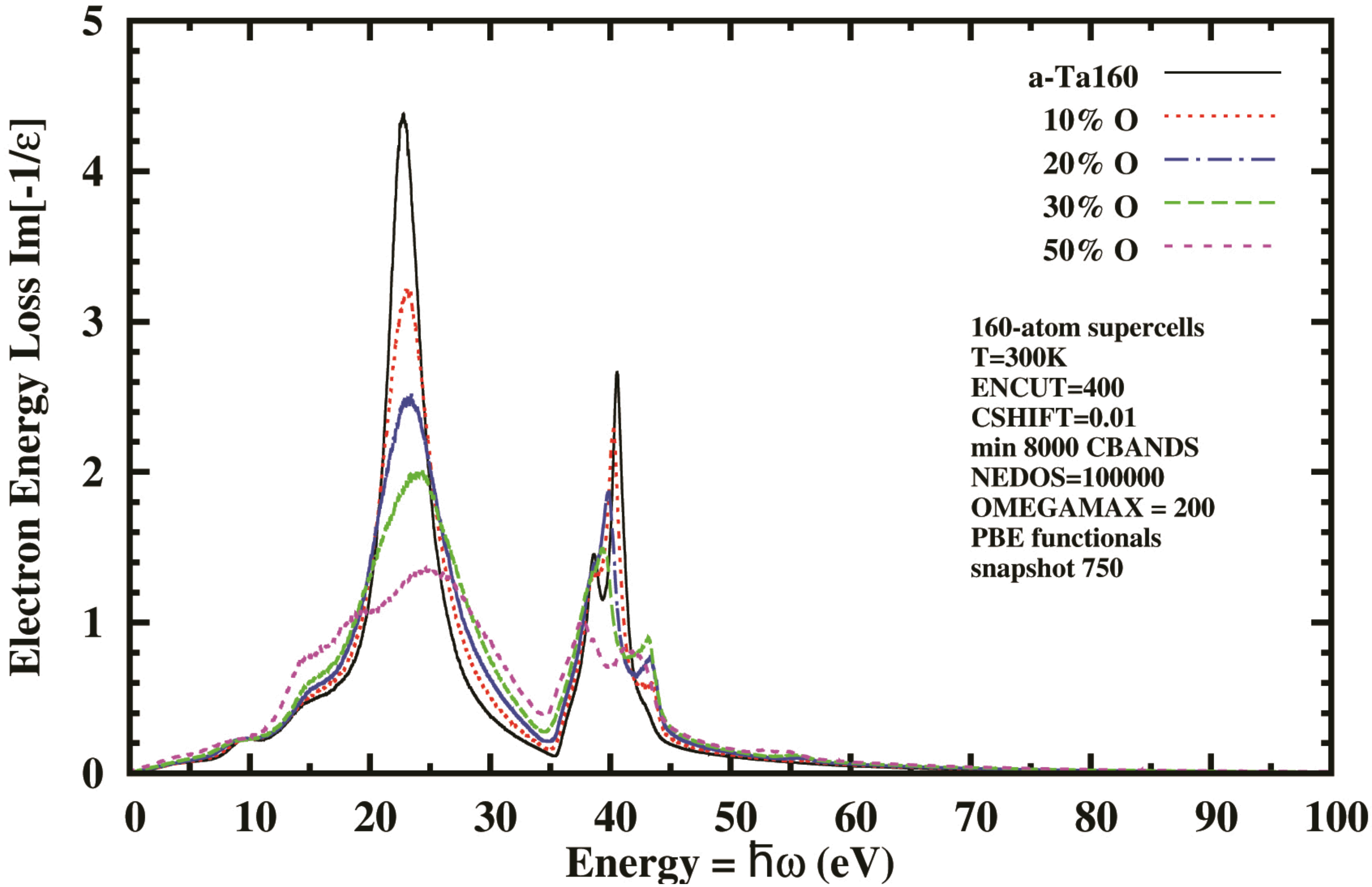
On and off states result in TaO_x becomes more metallic. Again, there is no indication of filament or channel formation.

Ta $O_{2,3}$-Oxidized, W $O_{2,3}$-metal



On and off states see formation of a more-insulating layer between TaO_x and Ta.

DFT: Amorphous Ta(O) Derivatives



- Qualitative trends are very clear with increasing O content (50% O is a-$Ta_{80}O_{80}$ or TaO). As O content increases:
  - Ta plasmon peak near 21 eV decreases and blueshifts.
  - Peak near 40 eV decreases and redshifts.
  - New peak grows below 45 eV.
  - Shoulder between 15 and 20 eV becomes more prominent.

Conclusions

- Used NEXAFS acquired data to analyze aged O-ring material
  - Used peak fitting to insinuate an explanation for ageing details
  - Model suggests ageing influences on C=C bond energies
- Implemented a fast multivariate method of peak fitting for EELS data
  - Capable of fitting many spectra simultaneously
  - Applied to multiple images simultaneously
- This preliminary analysis of Pt/TaO_x/Ta stack shows no filament formation after electrical challenge
  - This work indicates a possible resistance change across the TaO_x/Ta interface

Acknowledgements

- J.A. “Tony” Ohlhausen, Sandia National Laboratories, NEXAFS
- Daniel Fischer, National Institute of Standards & Technology
- Cherno Jaye, National Institute of Standards & Technology
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- Mat Celina, Sandia National Laboratories, polymer data interpretation
- Robert Bondi, Sandia National Laboratories, DFT
- Michael Rye, Sandia National Laboratories, FIB