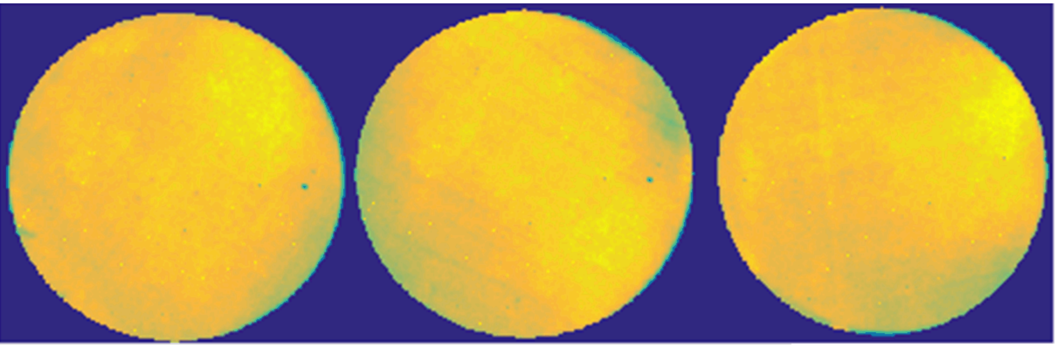
SAND2014-19536C

*Exceptional service in the national interest*

Sandia National Laboratories



# Global Analysis Peak Fitting for Imaging NEXAFS Data


Mark H. Van Benthem and James A. (Tony) Ohlhausen

Materials Science Research Division, Sandia National Laboratories


Chemical Imaging in 2D and 3D, 2014.11.12 1140

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration


Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

# Overview

- NSLS
  - Beamline U7A
- NEXAFS (*a.k.a.* XANES)
  - Near Edge X-ray Absorption Fine Structure
  - Spectroscopy
  - Imaging
  - Data Arrays
- Multivariate Analysis
  - Peak Fitting
  - Least Squares
  - Principal Component Analysis (PCA)
- Analysis of O-ring polymer material

# Motivation

Sandia National Laboratories

- Interested primarily in investigating how NEXAFS can help elucidate materials ageing
- NEXAFS gives information about bonds in various types of materials including organics
- Peak fitting can help elucidate the nature of bonding in polymers
- Typically, peak fitting is performed on a single spectrum
- Fitting NEXAFS images, multiple spectra simultaneously, can provide information about the areal extent of bonding in the material as well as mixed species

# National Synchrotron Light Source (NSLS)

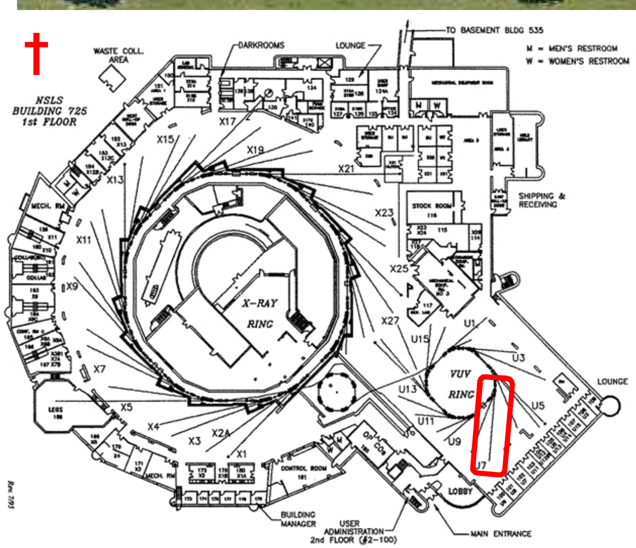
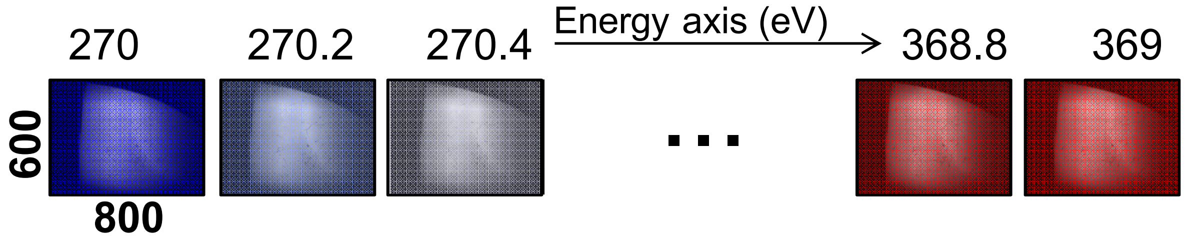



**Image Sources: * www.bnl.gov and †cdac.carnegiescience.edu**

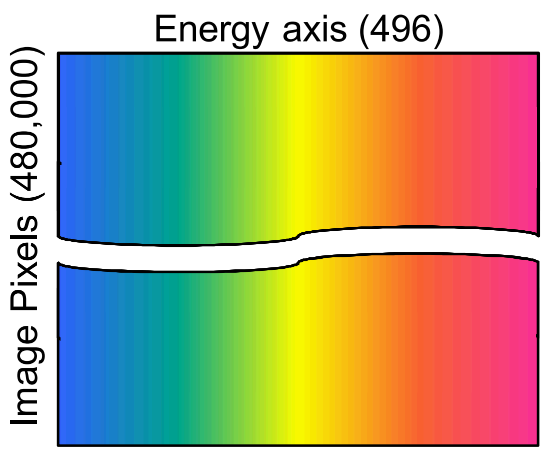
# NEXAFS Data Arrays

- Consider a collection of Imaging NEXAFS data




600×800×496

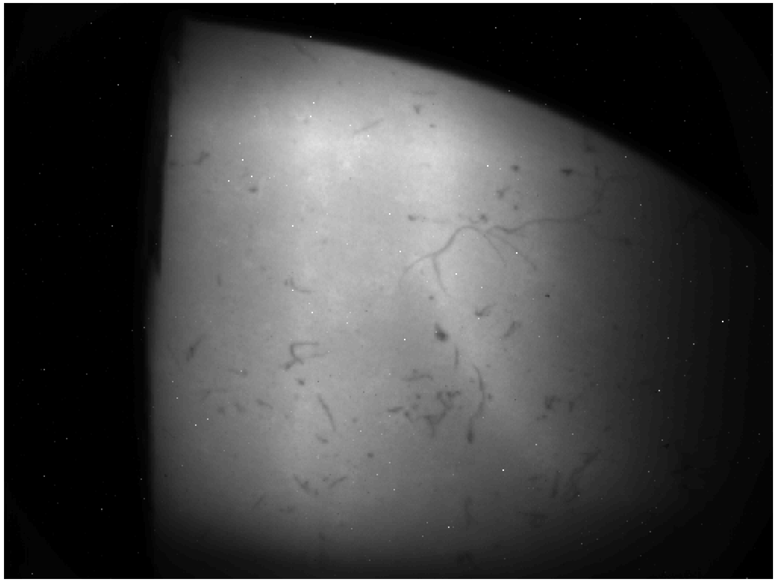
- These data can be reorganized as a matrix by stringing out the images as a vector of pixels



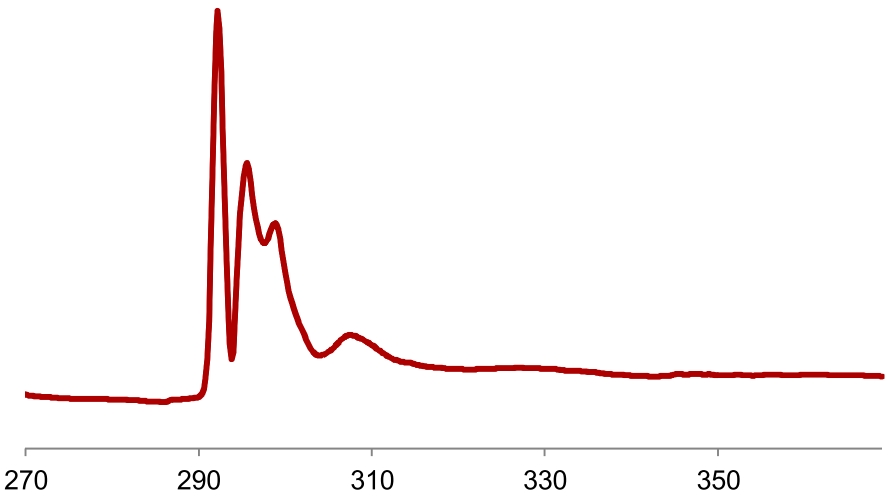

= **D**

# Grayscale Image

- If we collapse $\mathrm{D}$ along the spectral dimension, we obtain the monochrome image.

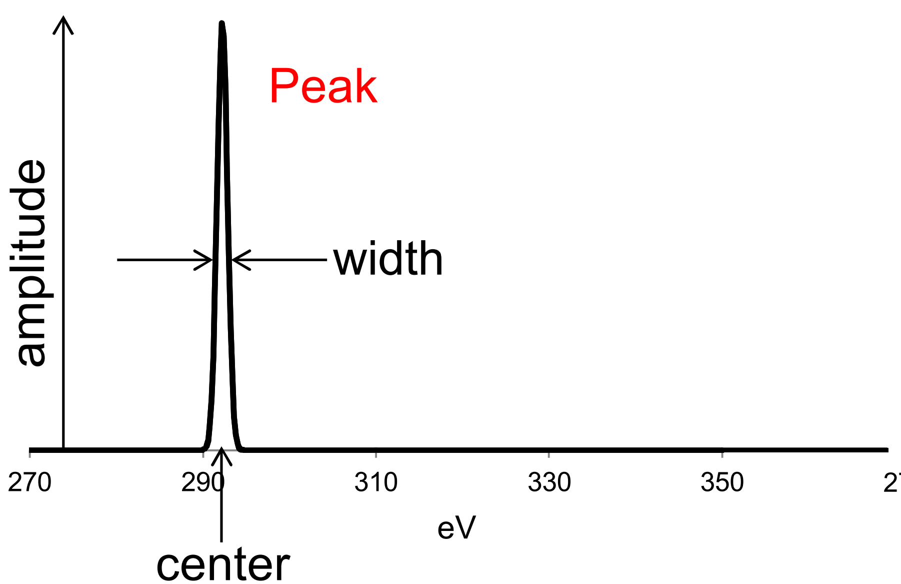


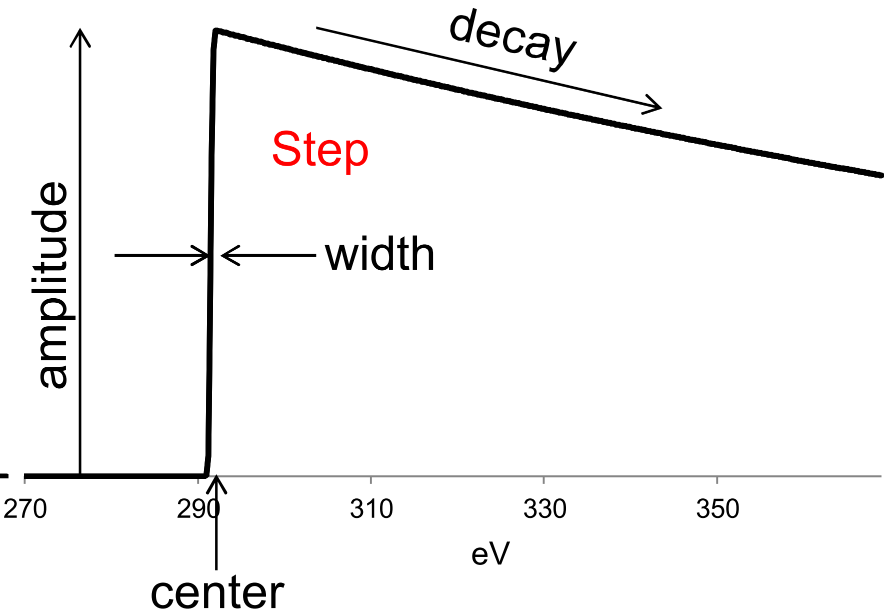
- If we collapse $\mathrm{D}$ along the image dimension we get the energy spectrum
  - Typically, users will curve fit this energy spectrum



# 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




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

# Peak, Step and Offset Definitions

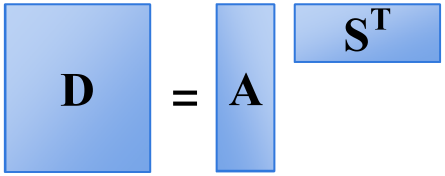
- Gaussian: $I_G = Ae^{-\left(\frac{E-E_0}{w}c\right)^2}$; where $c = 2\sqrt{\log 4}$
- Lorenztian: $I_L = A\left(\frac{(w/2)^2}{(E-E_0)^2+(w/2)^2}\right)$
- Pseudo-Voigt:

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

- 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

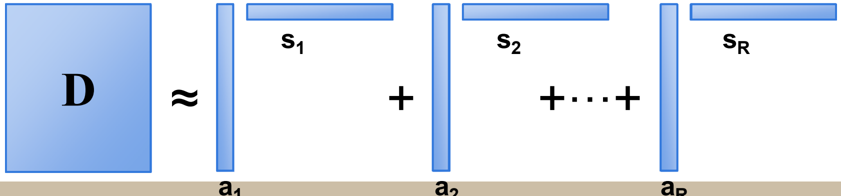
# Set Up the Least Squares Problem

- 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 $\mathrm{T}$ represents matrix transpose
- The least squares criterion: minimize $\left\|\mathbf{D} - \mathbf{A}\mathbf{S}^{\mathrm{T}}\right\|^2$

## Least Squares Model





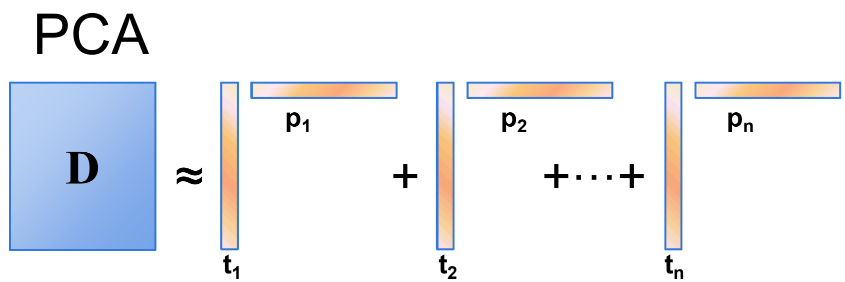
Knorr, F. J. and J. M. Harris, Analytical Chemistry **53(2):** 272-276, (1981).
Beechem, J. M., Numerical Computer Methods. L. Brand and M. L. Johnson, Methods in Enzymology San Diego, Academic Press. **210:** 37-54, (1992).

# Solving the Problem

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

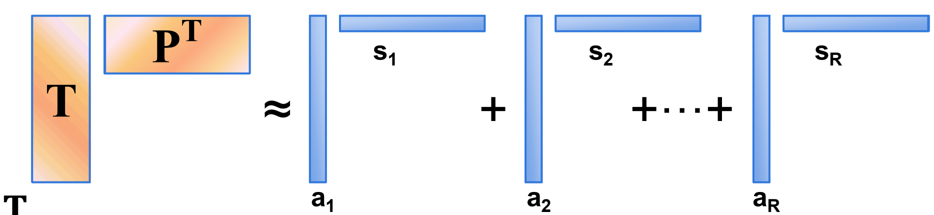
# Compression

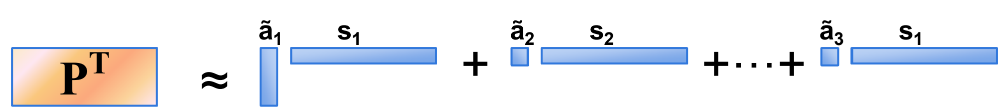
- We can represent the data as the product of two orthogonal matrices using principal component analysis (PCA): $\mathbf{D} = \mathbf{TP^T}$




  - $\mathbf{T}$ 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 $\mathbf{D} = \mathbf{AS^T}$
  - Now we can write $\mathbf{TP^T} = \mathbf{AS^T}$
  - Finally, we can define $\mathbf{P^T} = \tilde{\mathbf{A}}\mathbf{S^T}$

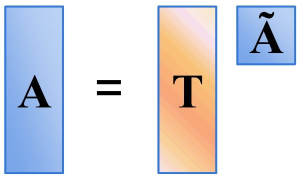



Henry, E. R. and J. Hofrichter, Numerical Computer Methods. L. Brand and M. L. Johnson, Methods in Enzymology San Diego, Academic Press. **210:** 129-192, (1992).

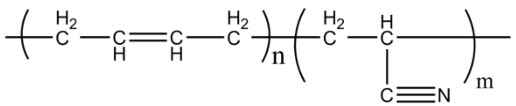
# Compression Use

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




- Nonnegativity can be imposed with only a minor computational penalty

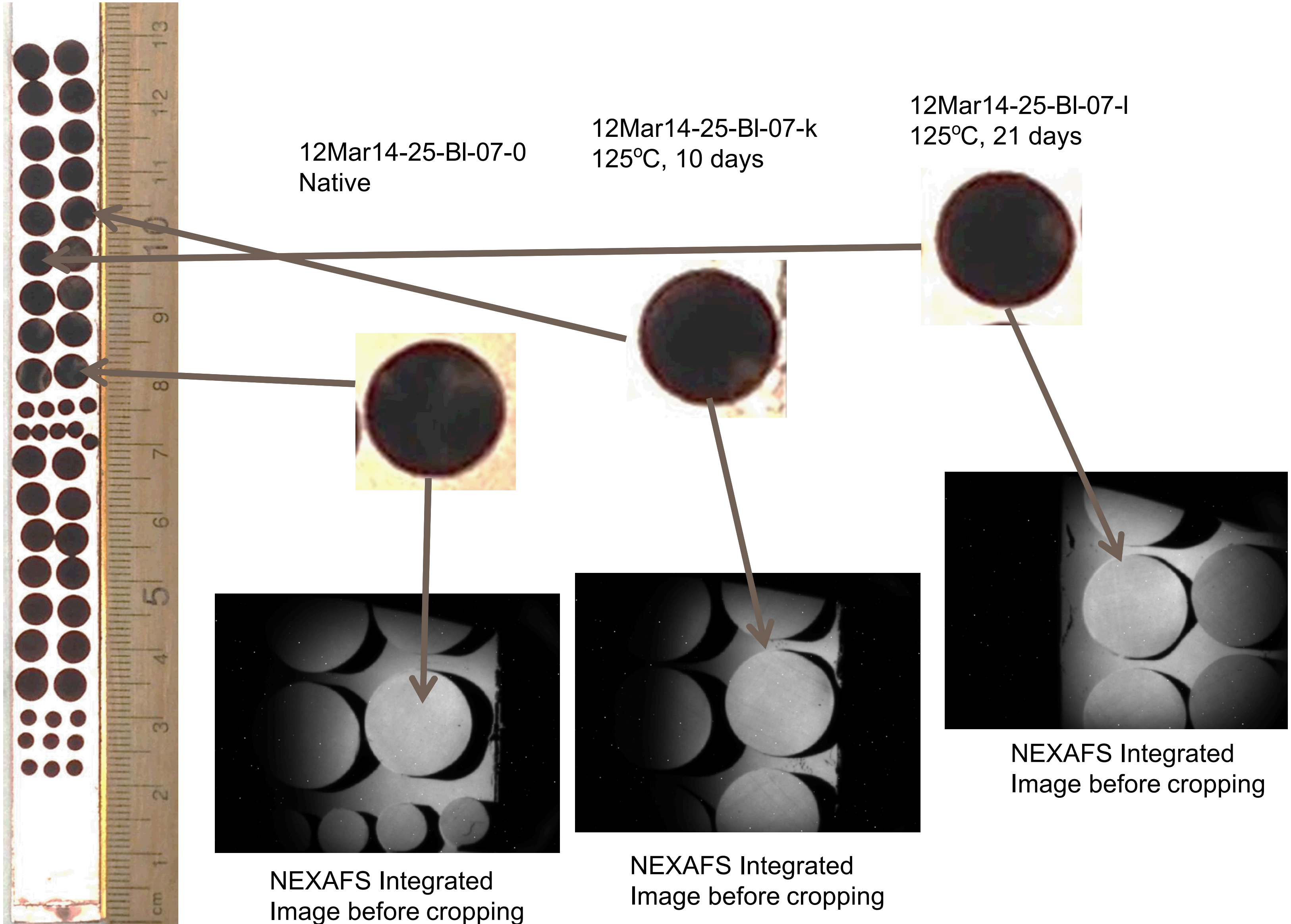
# Sample and Analysis Summary



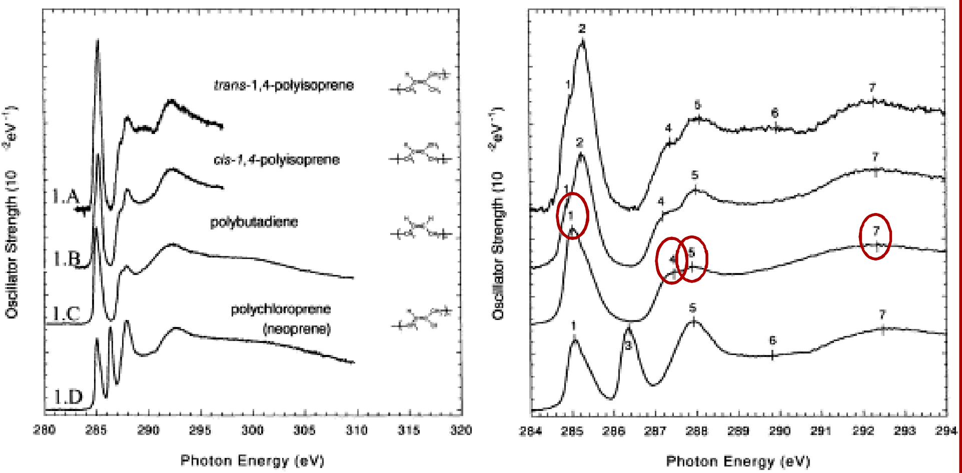
**Nitrile Rubber, Buna-N, Butadiene (from www.wikipedia.org)**

- 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$^{o}$C, 10 days
  - 125$^{o}$C, 21 days
- After aging, ~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

# Samples Analyzed



# Spectral Peak Assignments



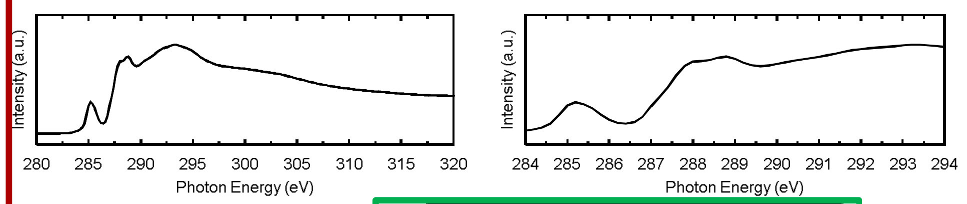

| # | Energy (eV) 1.A | 1.B | 1.C | 1.D | Assignment (optical orbital) C-H | C-C | C-Cl |
|---|---|---|---|---|---|---|---|
| 1 | 284.85 | 284.85 | 285.14 | 285.11 | $1\pi^*_{C=C}$ | | |
| 2 | 285.28 | 285.28 | | | | $1\pi^*_{C=C}$ | |
| 3 | | | | 286.37 | | | $1\pi^*_{C=C}$ |
| 4 | 287.18 | 287.15 |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

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

Fig. 3 (a) C 1s NEXAFS 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

## O-ring NEXAFS spectrum in this work



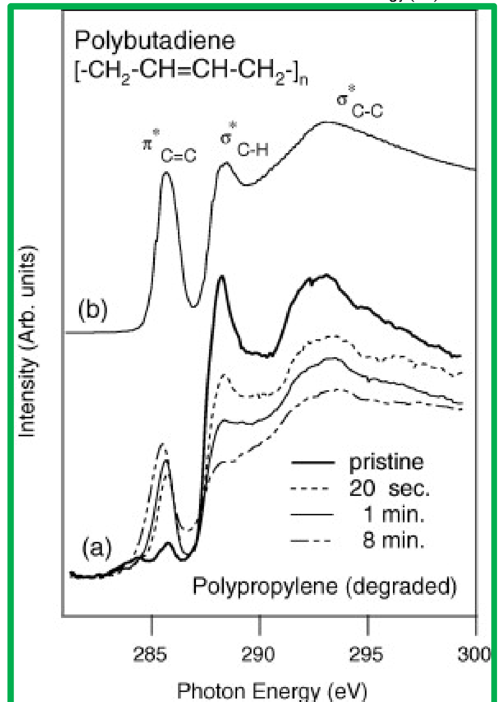
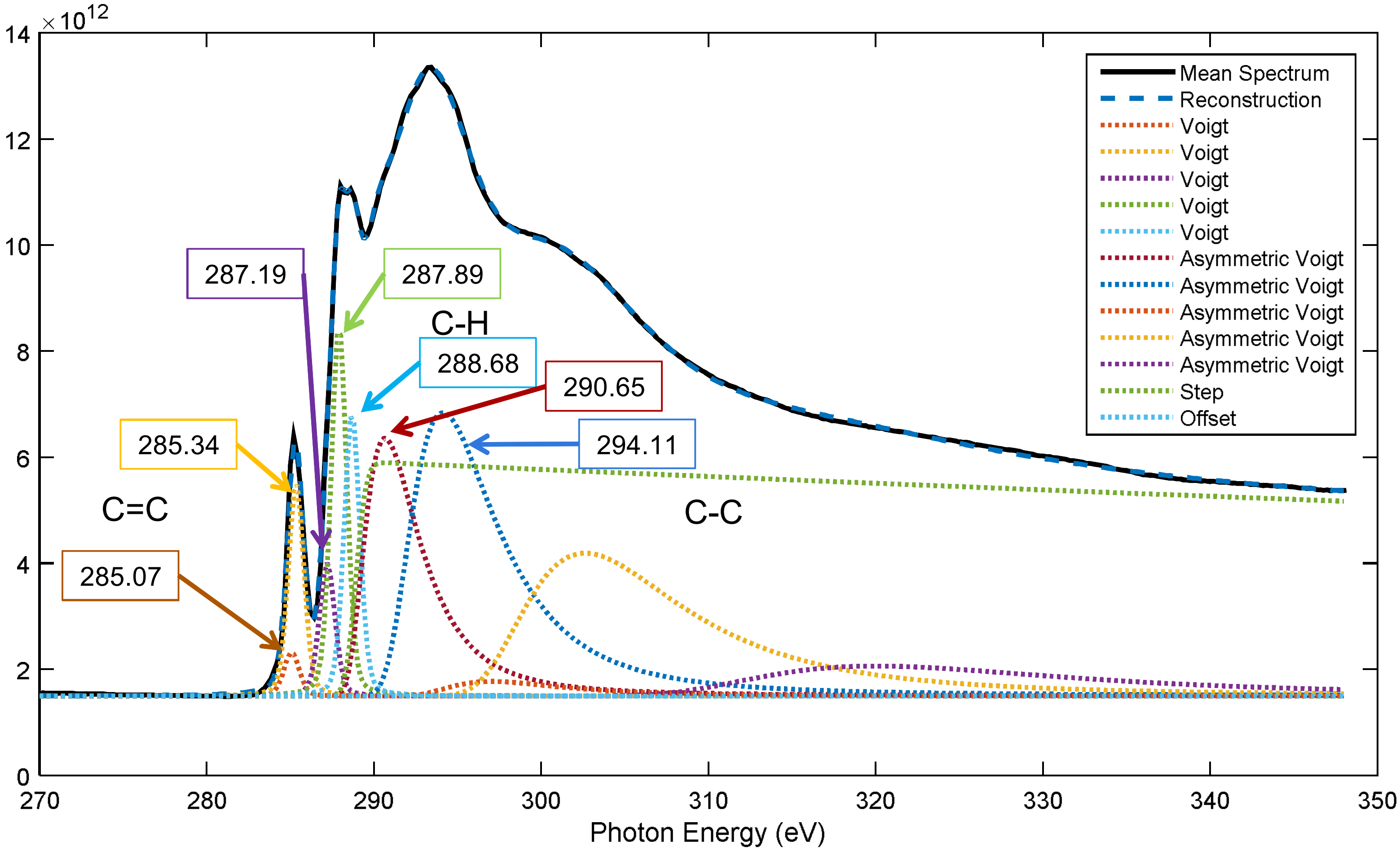



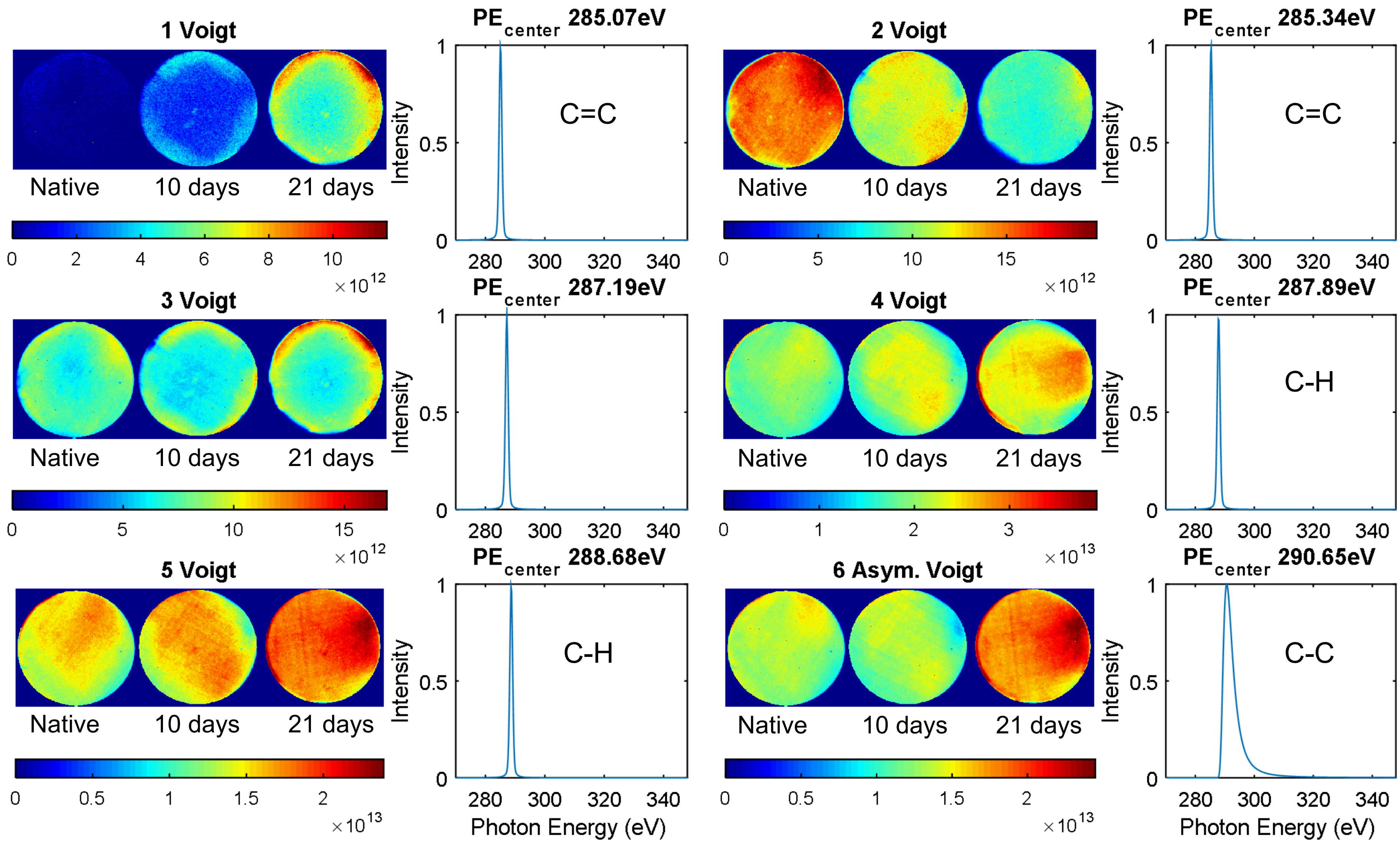

Fig. 5 (a) A series of carbon K-edge NEXAFS spectra of pristine and degraded polypropylene thin-films with different photon-irradiation time. (b) NEXAFS spectrum of polybutadiene polymer.

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

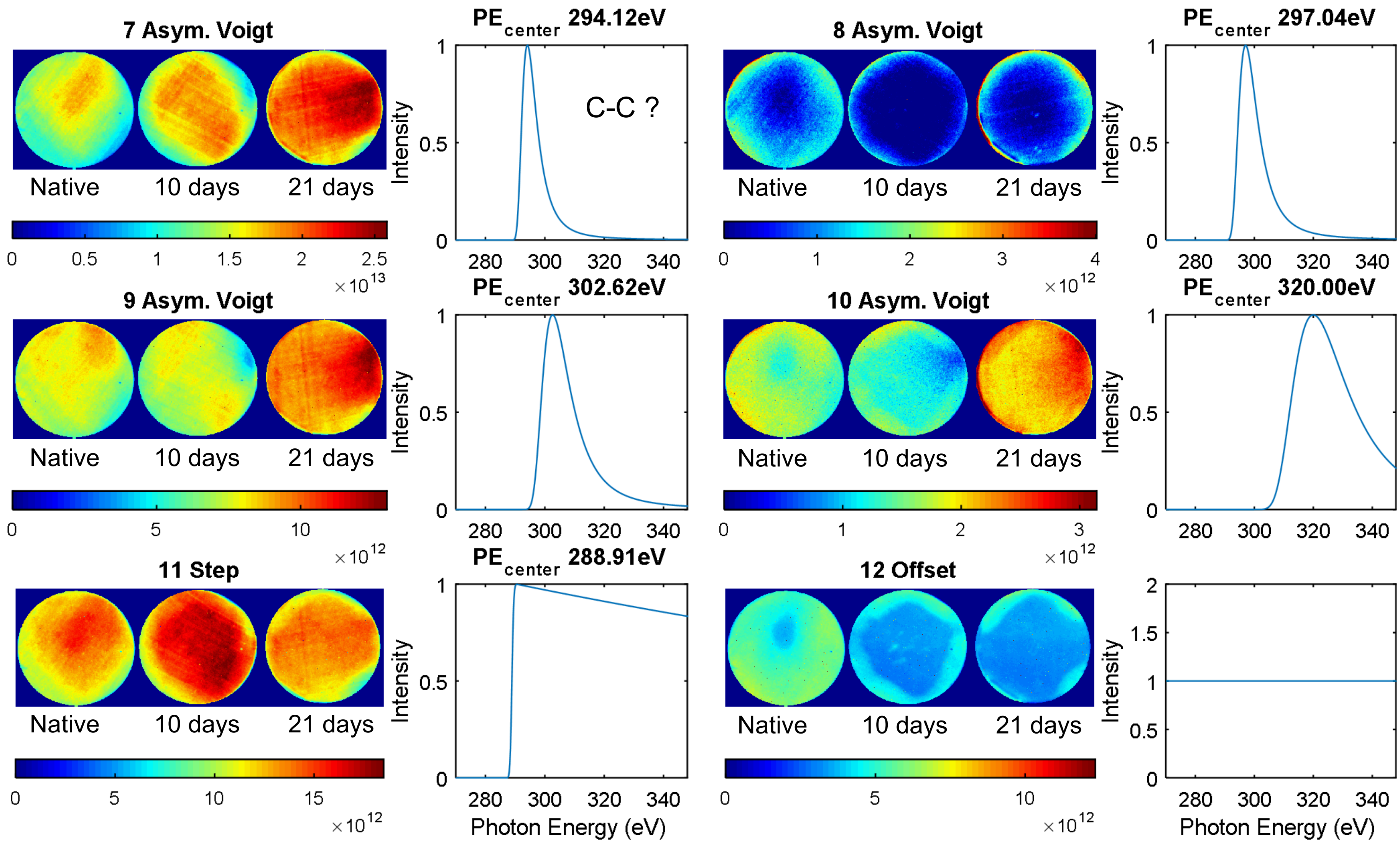
# Total Spectrum Fit



# Global Analysis Factors 1-6

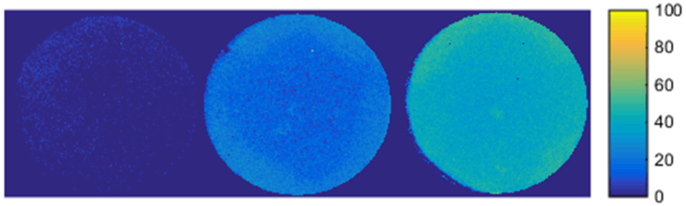


# Global Analysis Factors 7-12



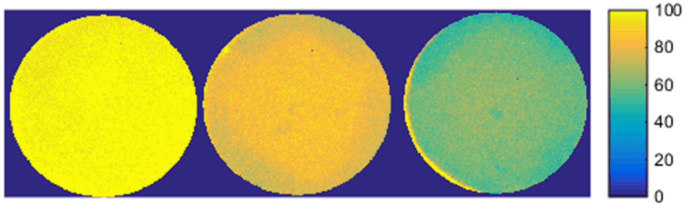
# Comparison of the C=C Voigt Peaks

**Percent Voigt 1 (of Voigt 1 and 2)**




Native 10 days 21 days

**Percent Voigt 2 (of Voigt 1 and 2)**




Native 10 days 21 days

# 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
- 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 advantage of image inhomogeneities during fitting process
  - Show promise for finding variation in the spatial domain to aid in data interpretation

# Acknowledgements


- Daniel Fischer, National Institute of Standards & Technology
- Cherno Jaye, National Institute of Standards & Technology
- National Synchrotron Light Source (NSLS) and Brookhaven National Laboratory (BNL)
- Sandia National Laboratories