Finding Specificity in Multivariate Curve Resolution

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Finding Specificity in Multivariate Curve Resolution

- Multivariate Curve Resolution (MCR)
- Simulated Evolution Example
  - Multiplicative Ambiguity
  - Rotational Ambiguity
  - Initial Guesses
- *Simple* Dissolution Example
- Conclusions

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Multivariate Curve Resolution

- MCR is most often used with spectra,
  - also known as self-modeling curve resolution, self-modeling mixture analysis, “end member extraction”
- Often used when you do NOT have calibration data
- Goal is to recover underlying "factors" which represent physically-identifiable features.

MCR

- Based on the classical least squares (CLS) model, attempt to estimate **C** and **S** given **X**:

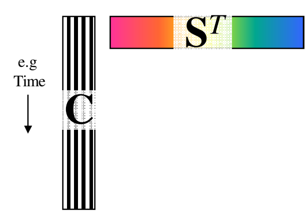
$$\mathbf{X} = \mathbf{C}\mathbf{S}^T + \mathbf{E}$$

X *M*x*N* measured responses,

C *M*x*K* pure analyte contributions,

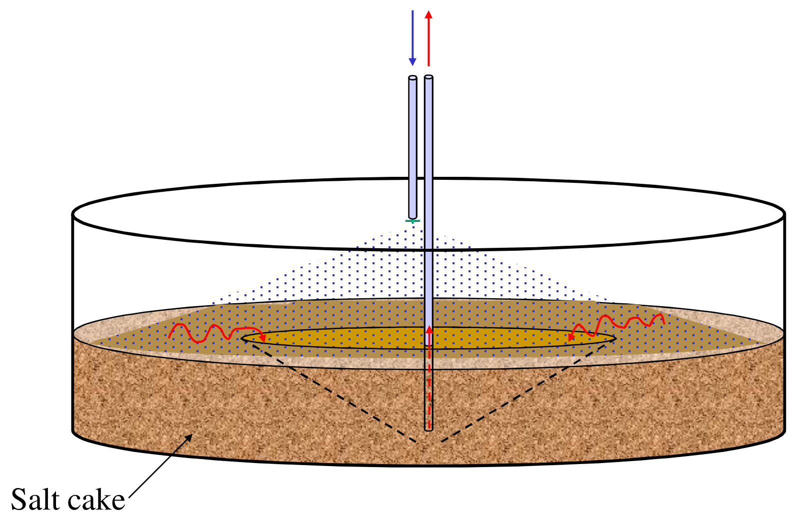
S *N*x*K* pure analyte spectra, and

E *M*x*N* residuals.

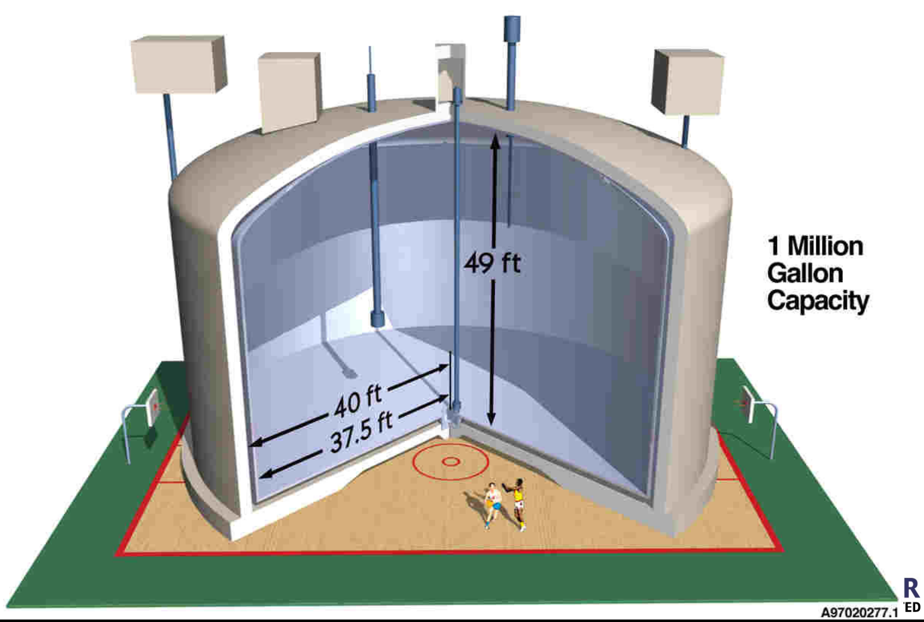


- Non-Negative Alternating Least Squares (NN-ALS)

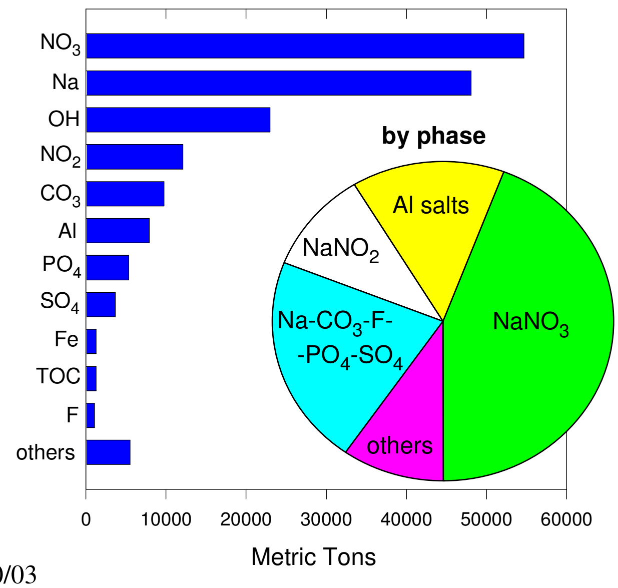
Nuclear Waste Storage Tanks



Hanford Double-Shell Tank

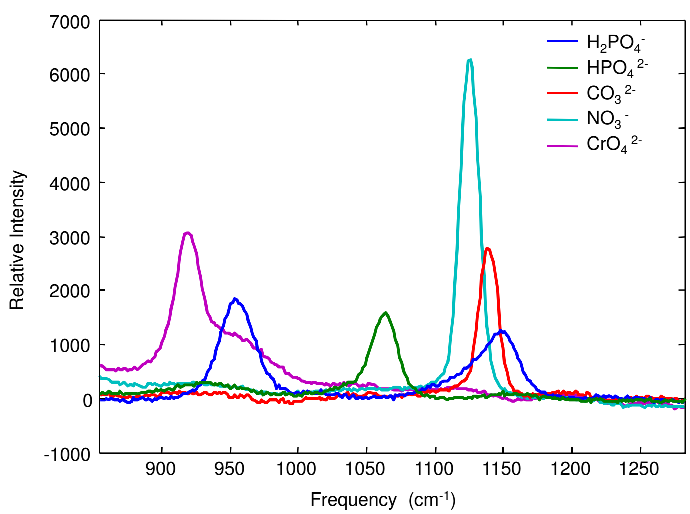


Tank Farm Chemical Inventory



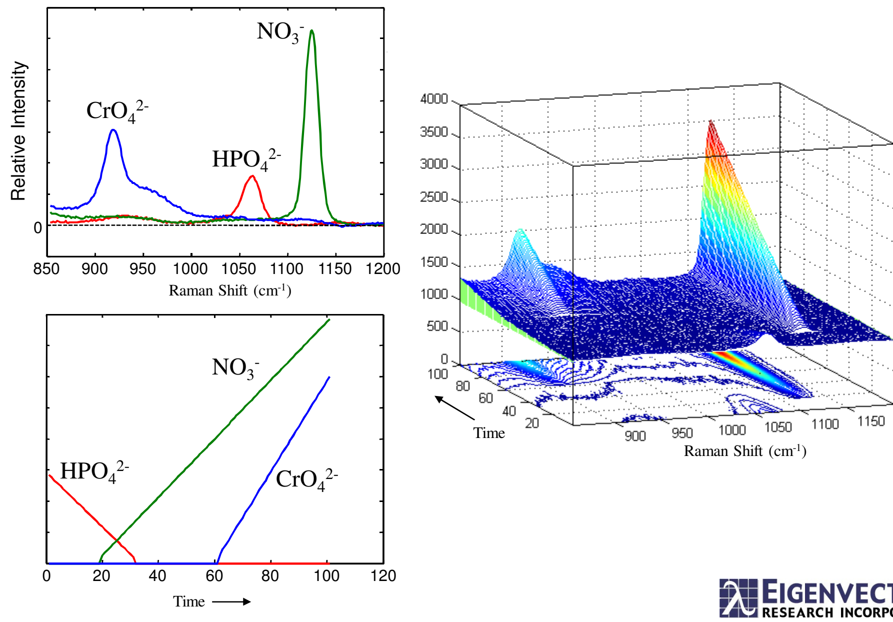
BBI 3/20/03

Raman Spectra of Ionic Species



Data courtesy Sam Bryan, Battelle (PNNL)

Simulated Evolution



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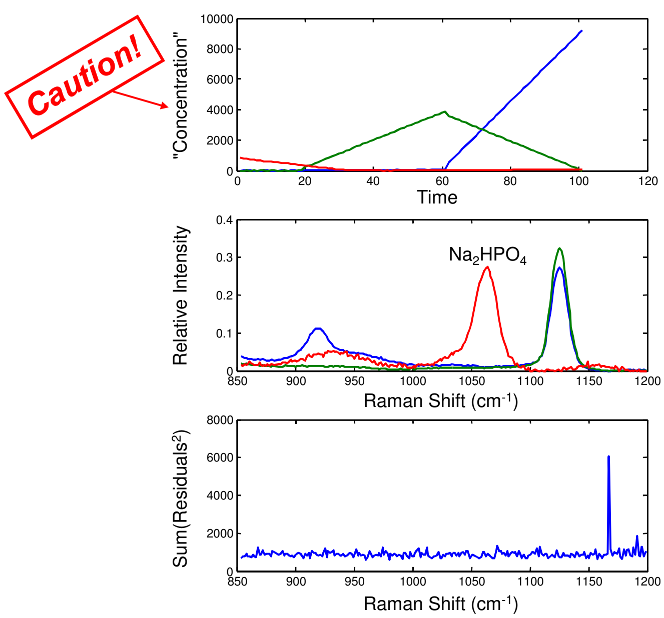
Multiplicative Ambiguity



Scores (C)

Factors (S)

Residuals (E)

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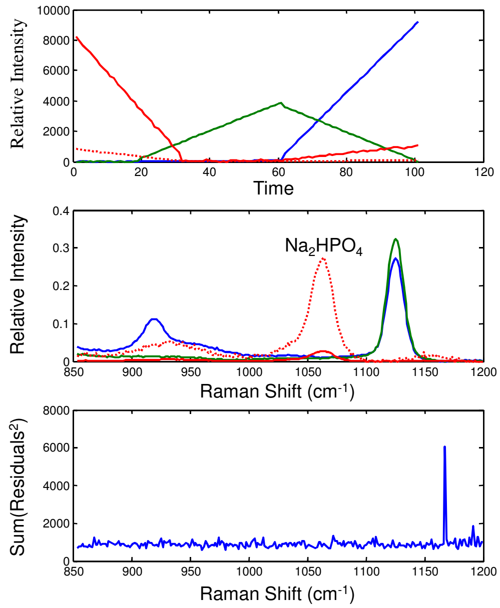
Multiplicative Ambiguity



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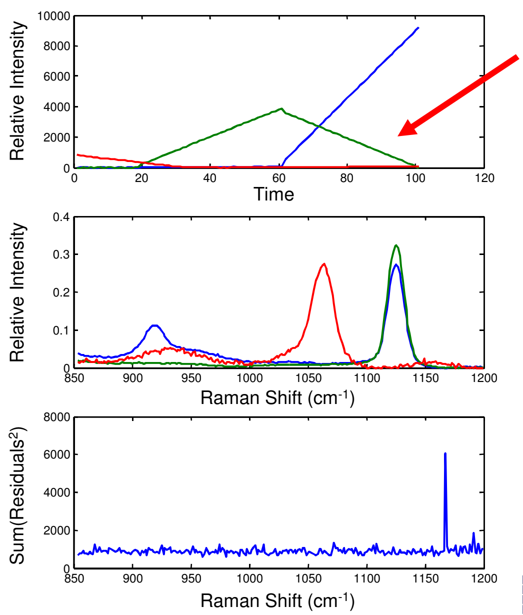
Rotational Ambiguity



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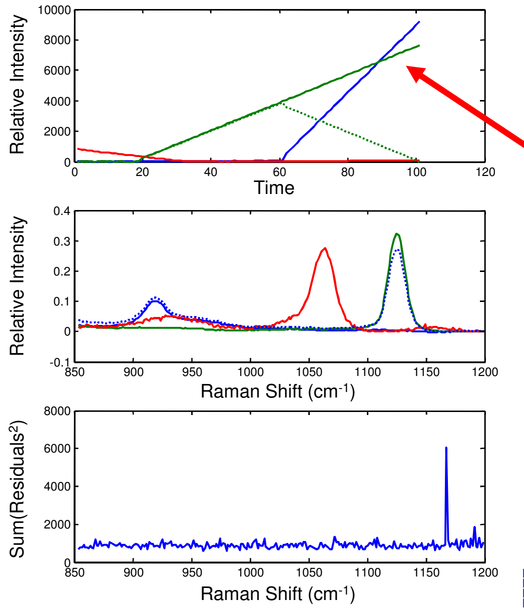
Rotational Ambiguity



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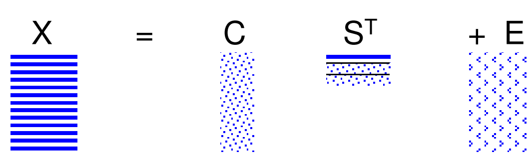
Ambiguity Work-Arounds

- **Fix factors** to pure spectra measured at known concentrations.

With all components, this → *CLS!* but must know species *a priori*

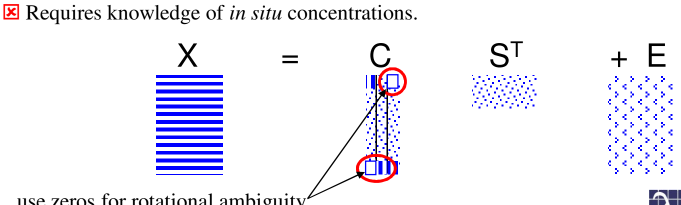
☒ Caution for matrix effects which change spectral profile (e.g. band shifts).



- **Fix contributions** at given times to known concentration values.

☑ Less sensitive to matrix effects

☒ Requires knowledge of *in situ* concentrations.



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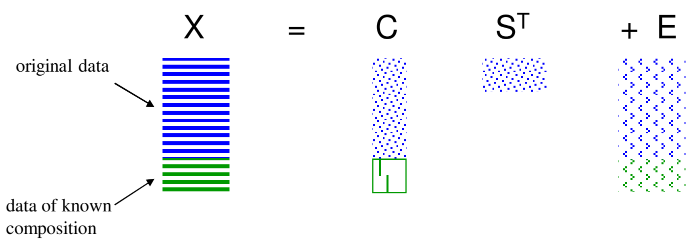
Ambiguity Work-Arounds

•**Add spectra** (at known concentrations) to data along with fixed concentrations.

- "Soft" constraint - allows some error "wiggle-room".



☑ Less sensitive to matrix effects on spectral shape
☒ Still sensitive to matrix effects on Scattering efficiency / absorbtivity

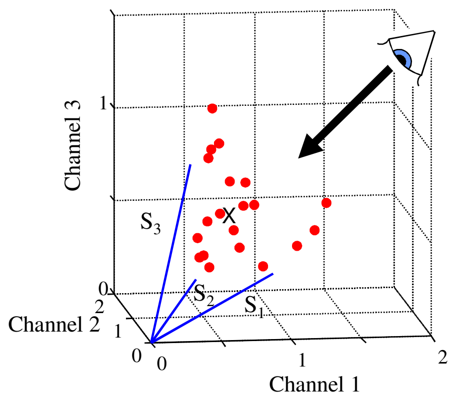
Ambiguity Work-Arounds

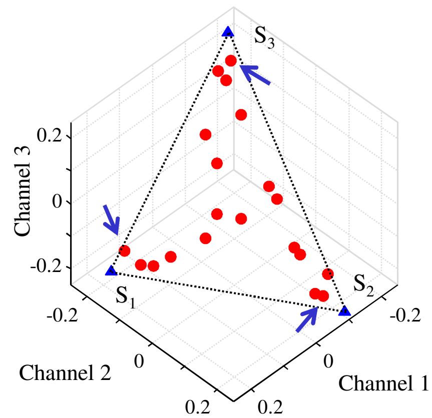
- **Multiplicative:** Use known chemical relationships to get *RELATIVE* concentrations (e.g. identification of species + order of reaction, or Closure)
- **Rotational:** Use expected simplicity of contribution profiles to direct solution towards simple explanation (e.g. unimodality).

☒ **All these methods:**
Unexpected components? *Interpret Carefully!*

Sum Scaled Intensity
Sum Scaled Current
Sum Scaled …

Initial Guess
"Pure[est] Samples"





— normalize + mean center →

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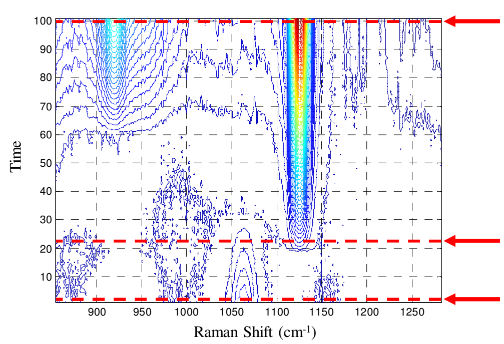
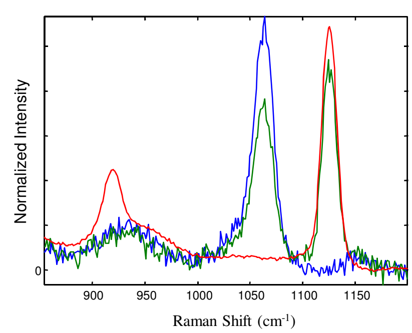
Initial Guess
"Pure[est] Samples"





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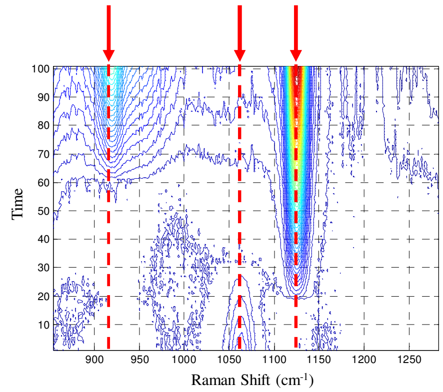
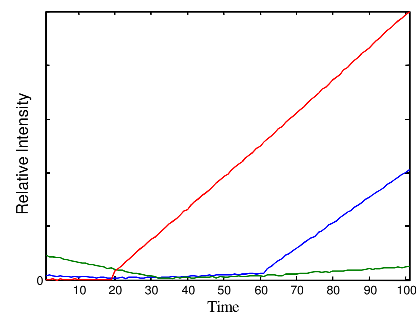
Initial Guess
"Pure[est] Variables"





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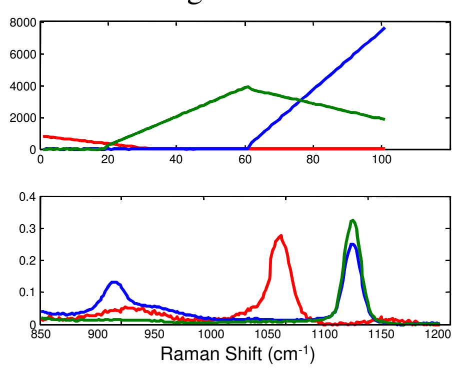
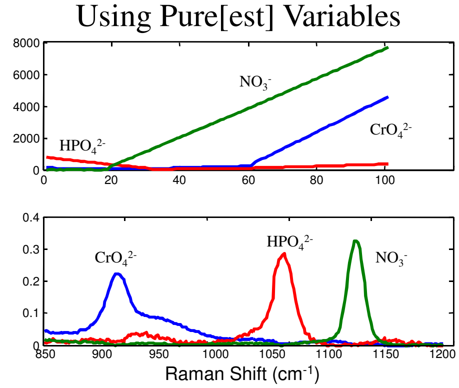
Initial Guess
"Pure[est] Variables"

Using PCA Scores



(similar to results with random starting vectors)

Using Pure[est] Variables



CrO_4^{2-} and HPO_4^{2-} were the spectrally difficult ones!

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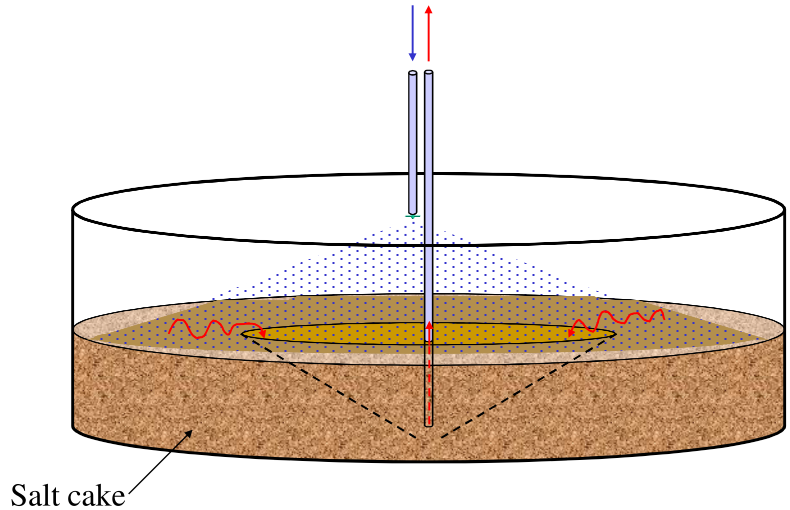
Nuclear Waste Storage Tanks



Simple Dissolution Simulation

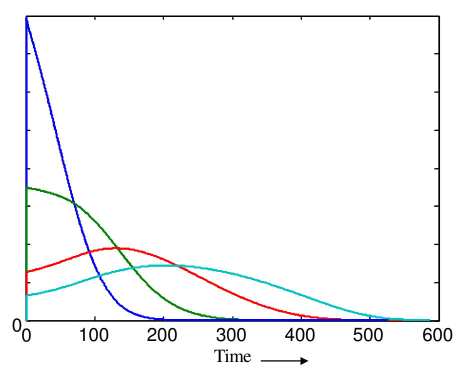
common ion — observed species

$$XA_{(s)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X^+ + A^- \xrightarrow{k_T} elution$$

$$XB_{(s)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X^+ + B^- \xrightarrow{k_T} elution$$

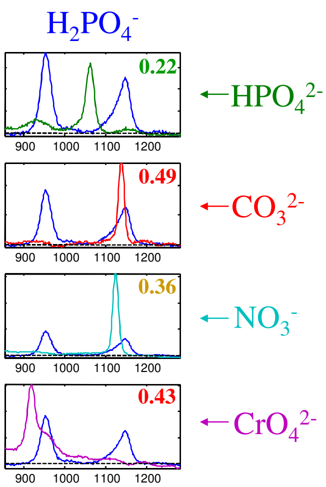
$$XC_{(s)} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} X^+ + C^- \xrightarrow{k_T} elution$$

$$XD_{(s)} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} X^+ + D^- \xrightarrow{k_T} elution$$



- Chemistry of species assigned to a given evolution profile does NOT necessarily match the equations above (e.g. HPO_4^{2-})
- Super-saturation effects (H-bonding) NOT included in model
- Ionic strength effects NOT included in model

Quantifying Spectral Overlap



1.00 = indistinguishable
0.00 = complete selectivity

$s_{1,norm} = ||s_1||$
$s_{2,norm} = ||s_2||$
$c = s_{1,norm} \bullet s_{2,norm}^T$

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Quantifying Spectral Overlap

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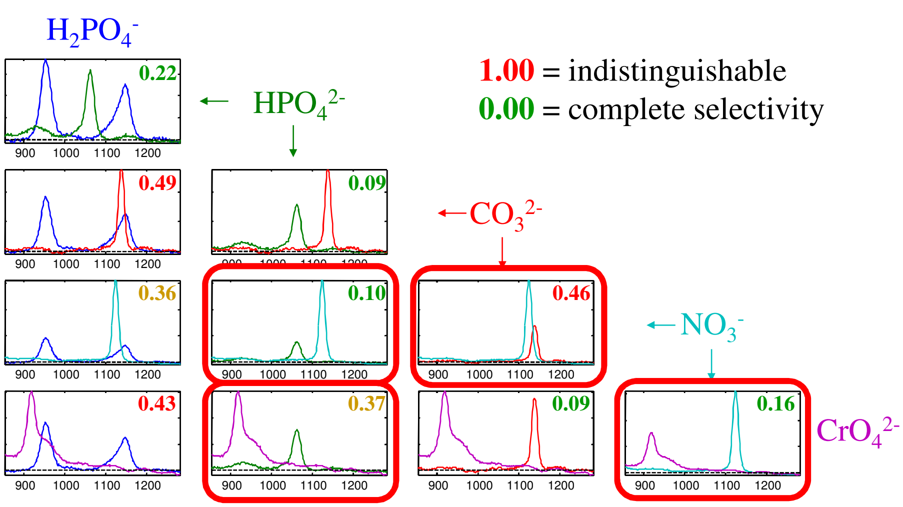

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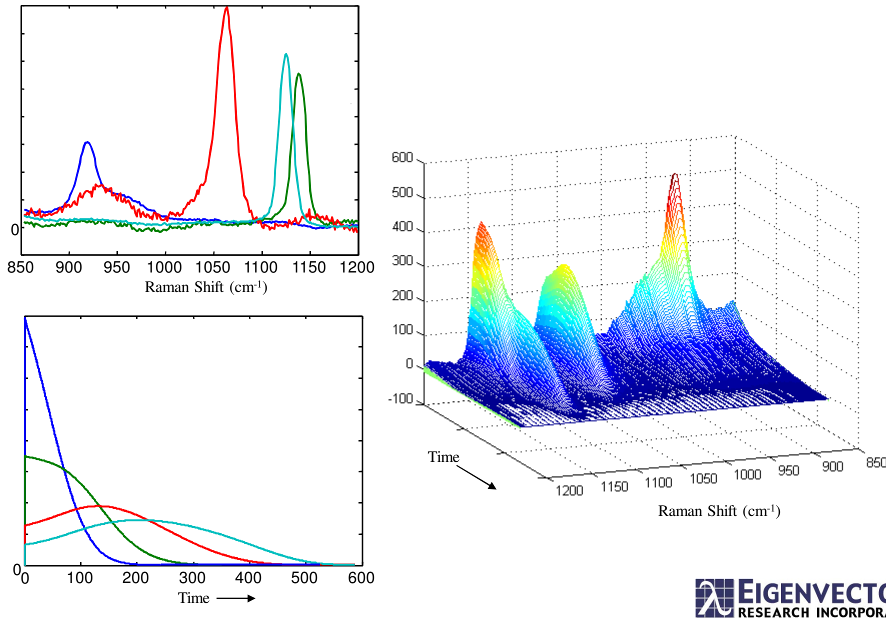
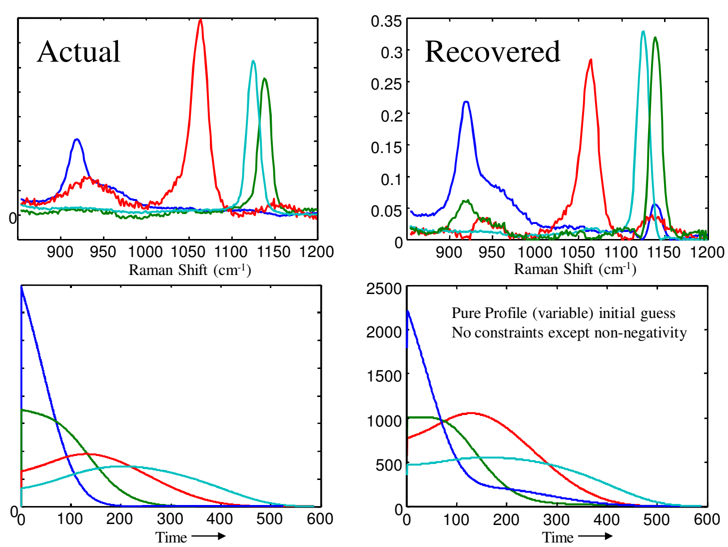
Simple Dissolution Simulation



Simple Dissolution Simulation



Conclusions

- A variety of hard and soft constraints exist to reduce effect of multiplicative and rotational ambiguities BUT
- Sometimes, just starting in the right neighborhood goes a long way!

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