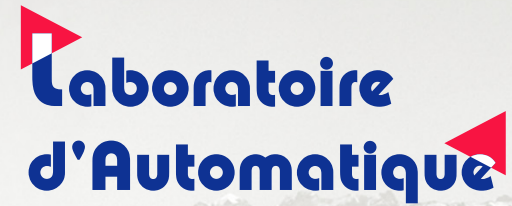




ÉCOLE POLYTECHNIQUE  
FÉDÉRALE DE LAUSANNE



# INCREMENTAL KINETIC MODELING OF SPECTROSCOPIC DATA USING A REDUCED CALIBRATION MODEL

Julien Billeter and Dominique Bonvin

Laboratoire d'Automatique  
Ecole Polytechnique Fédérale de Lausanne  
Switzerland

15<sup>th</sup> Scandinavian Symposium on Chemometrics  
June 21, 2017, Naantali (Finland)

# INTRODUCTION AND MOTIVATION

## Extent-based Incremental Kinetic Modeling

Decomposition of the identification problem into sub-problems:

- (i) transformation of  $\mathbf{C}$  to  $\mathbf{X}$ , and
- (ii) modeling of each individual extent,  $\mathbf{x}_i$ ,  $\forall i = 1, \dots, R$  reactions

Condition:  $S_a \geq R$

# INTRODUCTION AND MOTIVATION

## Extent-based Incremental Kinetic Modeling

Decomposition of the identification problem into sub-problems:

- (i) transformation of  $\mathbf{C}$  to  $\mathbf{X}$ , and
- (ii) modeling of each individual extent,  $\mathbf{x}_i$ ,  $\forall i = 1, \dots, R$  reactions

Condition:  $S_a \geq R$

## Reduced Calibration Model of Spectroscopic Data

For practical reasons, one wants to build a calibration model  $\mathbf{C}_a = \mathbf{f}(\mathbf{A})$  with a minimum number of species  $\rightarrow S_a < R$

# INTRODUCTION AND MOTIVATION

## Extent-based Incremental Kinetic Modeling

Decomposition of the identification problem into sub-problems:

- (i) transformation of  $\mathbf{C}$  to  $\mathbf{X}$ , and
- (ii) modeling of each individual extent,  $\mathbf{x}_i$ ,  $\forall i = 1, \dots, R$  reactions

Condition:  $S_a \geq R$

## Reduced Calibration Model of Spectroscopic Data

For practical reasons, one wants to build a calibration model  $\mathbf{C}_a = \mathbf{f}(\mathbf{A})$  with a minimum number of species  $\rightarrow S_a < R$

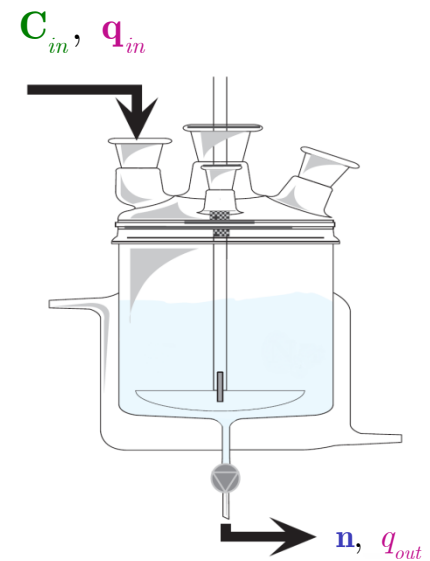
## Aim of this Work

Incremental kinetic modeling using a calibration model of spectroscopic data with a reduced set of species  $S_a < R$

# MATERIAL BALANCE EQUATIONS

Consider the material balance equations of a reaction system with

- $S_a$  (available) species
- $R$  reactions
- $p$  inlets
- 1 outlet



$$\dot{\mathbf{n}}_a(t) = \mathbf{N}_a^T \mathbf{r}_v(t) + \mathbf{C}_{in,a} \mathbf{q}_{in}(t) - \omega(t) \mathbf{n}_a(t), \quad \mathbf{n}_a(0) = \mathbf{n}_{0,a}$$

$S_a$        $S_a \times R$     $R$        $S_a \times p$     $p$        $1$        $S_a$        $S_a$

with  $\omega(t) := \frac{q_{out}(t)}{V_{out}(t)}$  and  $\mathbf{r}_v(t) = V(t) \mathbf{r}(t)$

# INCREMENTAL KINETIC MODELING

The kinetic problem is decomposed into sub-problems of lower dimension and complexity.

The extent-based incremental kinetic modeling proceeds in **two steps**:

## I. Transformation to extents

Computation of the contribution of each reaction in the form of an extent (+ state reconstruction of the unmeasured numbers of moles, if necessary)

## II. Model identification (parameter estimation)

Modeling of each individual rate expression from its corresponding extent

# INCREMENTAL KINETIC MODELING

## I. Transformation to extents

i. Computation of  $p$  extents of inlet and 1 extent of initial conditions:

$$\begin{aligned}\dot{\mathbf{x}}_{in}(t) &= \mathbf{q}_{in}(t) - \boldsymbol{\omega}(t) \mathbf{x}_{in}(t), & \mathbf{x}_{in}(0) &= \mathbf{0}_p & \Rightarrow \mathbf{x}_{in}(t) &= \int_0^t \dot{\mathbf{x}}_{in}(\tau) d\tau \\ \dot{x}_{ic}(t) &= -\boldsymbol{\omega}(t) x_{ic}(t), & x_{ic}(0) &= 1 & \Rightarrow x_{ic}(t) &= \int_0^t \dot{x}_{ic}(\tau) d\tau\end{aligned}$$

ii. Computation of the reaction-variant ( $vRV$ ) form of the measurements:

$$\tilde{\mathbf{n}}_a^{vRV}(t) = \mathbf{N}_a^T \tilde{\mathbf{x}}_r(t) = \tilde{\mathbf{n}}_a(t) - \mathbf{C}_{in,a} \mathbf{x}_{in}(t) - \mathbf{n}_{0,a} x_{ic}(t)$$

iii. Computation of the  $R$  extents of reaction:  $\tilde{\mathbf{x}}_r(t) = (\mathbf{N}_a^T)^+ \tilde{\mathbf{n}}_a^{vRV}(t)$

$$\text{with } \dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \boldsymbol{\omega}(t) \mathbf{x}_r(t), \quad \mathbf{x}_r(0) = \mathbf{0}_R$$

**Condition:**

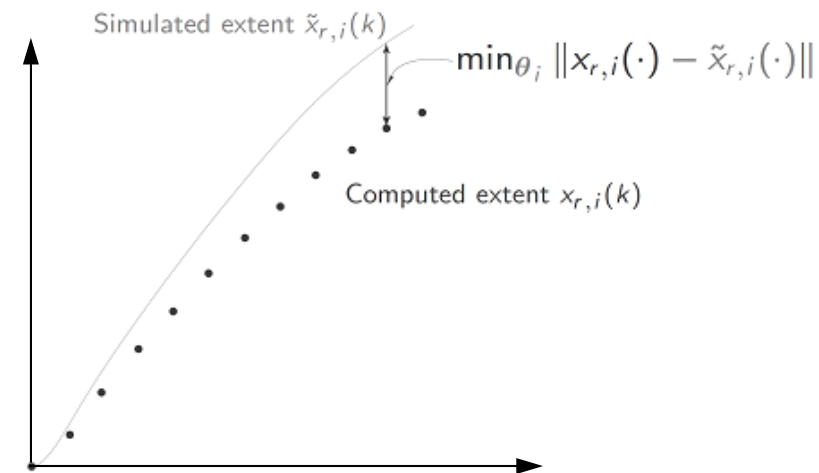
$$\text{rank}(\mathbf{N}_a) = R \Rightarrow S_a \geq R$$

# INCREMENTAL KINETIC MODELING

## II. Model identification

A rate expression is postulated for each extent of reaction, and **each identification problem is solved separately** by comparing the corresponding measured and modeled extent:

$$\begin{aligned} \min_{\theta_{r,i}} \quad & \left\| \tilde{x}_{r,i}(t) - x_{r,i}(t) \right\|_W^2 & i = 1, \dots, R \\ \text{s.t.} \quad & \dot{x}_{r,i}(t) = r_{v,i}(\tilde{c}(t), \theta_{r,i}) - \omega(t)x_{r,i}(t), \\ & x_{r,i}(0) = 0 \\ & \underline{\theta}_{r,i} \leq \theta_{r,i} \leq \bar{\theta}_{r,i} \end{aligned}$$





# INCREMENTAL KINETIC MODELING

$$S_a < R$$

Two approaches are possible to adapt the incremental kinetic modeling to the case  $S_a < R$  i.e., when there are less measured species than reactions:

## 1. COMBINED DYNAMIC MODELING AND STATIC RECONSTRUCTION

- i. Some reaction extents ( $\mathbf{x}_{r,1}$ ) are **modeled dynamically** using candidate rate expressions and their rate parameters are **estimated simultaneously**
- ii. The remaining extents ( $\mathbf{x}_{r,2}$ ) are **reconstructed statically** from  $\tilde{\mathbf{n}}_a^{vRV}$  and  $\mathbf{x}_{r,1}$ , and their rate expressions are **identified incrementally**

## 2. SIMULTANEOUS IDENTIFICATION OF REACTION SUBSYSTEMS

- i. Some extents of reaction are **computed statically** from  $\tilde{\mathbf{n}}_a^{vRV}$
- ii. One determines the **subsets of reactions** whose rate expressions can be **identified separately between subsets** but **simultaneously within each subset**

# INCREMENTAL KINETIC MODELING ( $S_a < R$ )

## 1. Dynamic modeling / Static reconstruction

- i. Definition of  $\tilde{\mathbf{n}}_a^{vRV}$  in terms of two types of reaction extents ( $\mathbf{x}_{r,1}$ ,  $\mathbf{x}_{r,2}$ )

$$\tilde{\mathbf{n}}_a^{vRV}(t_h) = \mathbf{N}_{a,1}^T \mathbf{x}_{r,1}(t_h) + \mathbf{N}_{a,2}^T \mathbf{x}_{r,2}(t_h)$$

- ii. **Static reconstruction** of  $\mathbf{x}_{r,2}$  in terms of  $\tilde{\mathbf{n}}_a^{vRV}$  and  $\mathbf{x}_{r,1}$  (substitute  $\mathbf{x}_{r,2}$ )

$$\mathbf{n}_a^{vRV}(t_h) = \mathcal{A}_a \mathbf{x}_{r,1}(t_h) + \mathcal{B}_a \tilde{\mathbf{n}}_a^{vRV}(t_h)$$

with  $\mathcal{A}_a = (\mathbf{I}_{S_a} - \mathcal{B}_a) \mathbf{N}_{a,1}^T$ ,  $\mathcal{B}_a = \mathbf{N}_{a,2}^T (\mathbf{N}_{a,2}^T)^+$  and  $\boxed{\text{rank}(\mathbf{N}_{a,2}) < S_a \Rightarrow R_2 < S_a}$

- iii. Reconstruction of the unmeasured states  $\hat{\mathbf{n}}_a$  using  $\tilde{\mathbf{n}}_a^{vRV}$ ,  $\mathbf{x}_{r,1}$ ,  $\mathbf{x}_{in}$  and  $x_{ic}$

# INCREMENTAL KINETIC MODELING ( $S_a < R$ )

## 1. Dynamic modeling / Static reconstruction

**1A. SIMULTANEOUS IDENTIFICATION** of the  $R_1$  reactions from  $\mathbf{x}_{r,1}$

$$\begin{aligned} \min_{\boldsymbol{\theta}_{r,1}} \quad & \left\| (\mathbf{I}_{S_a} - \mathcal{B}_a) \tilde{\mathbf{n}}_a^{vRV}(t_h) - \mathcal{A}_a \mathbf{x}_{r,1}(t_h) \right\|_W^2 \quad \forall h = 1, \dots, H \\ \text{s.t.} \quad & \dot{\mathbf{x}}_{r,1}(t) = \mathbf{r}_{v,1}(\tilde{\mathbf{c}}(t), \boldsymbol{\theta}_{r,1}) - \boldsymbol{\omega}(t) \mathbf{x}_{r,1}(t), \quad \mathbf{x}_{r,1}(0) = \mathbf{0}_{R_1} \\ & \hat{\mathbf{n}}_u(t_h) = \mathcal{A}_u \mathbf{x}_{r,1}(t_h) + \mathcal{B}_u \tilde{\mathbf{n}}_a^{vRV}(t_h) + \mathbf{C}_{in,u} \mathbf{x}_{in}(t_h) + \mathbf{n}_{0,u} x_{ic}(t_h) \end{aligned}$$

**STATIC RECONSTRUCTION** of  $\mathbf{x}_{r,2}$  from  $\mathbf{x}_{r,1}$

$$\begin{aligned} \hat{\mathbf{x}}_{r,2}(t_h) &= (\mathbf{N}_{a,2}^T)^+ \tilde{\mathbf{n}}_a^{vRV}(t_h) - (\mathbf{N}_{a,2}^T)^+ \mathbf{N}_{a,1}^T \mathbf{x}_{r,1}(t_h) \\ R_2 < S_a & \qquad \qquad \qquad S_a \qquad \qquad \qquad R_1 \end{aligned}$$

**1B. INCREMENTAL IDENTIFICATION** of the  $R_2$  reactions from  $\mathbf{x}_{r,2}$

$$\begin{aligned} \min_{\boldsymbol{\theta}_{r,2,i}} \quad & \left\| \hat{x}_{r,2,i}(t_h) - x_{r,2,i}(t_h) \right\|_W^2 \quad \forall h = 1, \dots, H, \quad \forall i = 1, \dots, R_2 \\ \text{s.t.} \quad & \dot{x}_{r,2,i}(t) = r_{v,2,i}(\tilde{\mathbf{c}}(t), \boldsymbol{\theta}_{r,2,i}) - \boldsymbol{\omega}(t) x_{r,2,i}(t), \quad x_{r,2,i}(0) = 0 \end{aligned}$$

# INCREMENTAL KINETIC MODELING ( $S_a < R$ )

## 2. Simultaneous identification of subsystems

- i. Definition of  $S_a < R$  observable extents  $\mathbf{x}_r^\circ$  as

$$\mathbf{x}_r^\circ(t) = \mathbf{S}^T \mathbf{x}_r(t), \quad \text{s.t. } \mathbf{N}_a^T (\mathbf{S}^T \mathbf{S}) = \mathbf{N}_a^T \quad \text{and} \quad \mathbf{S}^T \mathbf{S} \neq \mathbf{I}_R$$

$\mathbf{S}$  constructed as  $\text{rref}(\mathbf{N}_a^T)$ , and removing the rows with either no or more than one non-zero elements.

- ii. Computation of the reaction-variant ( $vRV$ ) form of the measurements:

$$\mathbf{n}_a^{vRV}(t) = \mathbf{N}_a^T \mathbf{x}_r(t) = \mathbf{N}_a^T \mathbf{S}^T \mathbf{x}_r^\circ(t)$$

- iii. Computation of the  $R^\circ$  observable extents:  $\tilde{\mathbf{x}}_r^\circ(t_h) = (\mathbf{N}_a^T \mathbf{S}^T)^+ \tilde{\mathbf{n}}_a^{vRV}(t_h)$

- iv. Partition of  $\mathbf{N}$  in  $\begin{bmatrix} \mathbf{N}^\circ \\ \mathbf{N}_u \end{bmatrix}$  and reconstruction of the  $S_u^\circ$  unmeasured observable states  $\hat{\mathbf{n}}_u^\circ(t_h)$  based on  $\mathbf{N}_u$  using  $\tilde{\mathbf{n}}_a^{vRV}$ ,  $\tilde{\mathbf{x}}_r^\circ$ ,  $\mathbf{x}_{in}$  and  $\mathbf{x}_{ic}$

# INCREMENTAL KINETIC MODELING ( $S_a < R$ )

## 2. Simultaneous identification of subsystems

### SUBSYSTEM IDENTIFICATION (directed bipartite graph)

1. Create a graph with nodes for extents and concentrations
2. For each pair  $(i, j)$ , if  $\mathbf{N}_{i,j} \neq 0$ , add a directed arc  $x_i \rightarrow n_j$
3. Label the arcs to **observable** conc. as **reconstruction arcs** ( $- \rightarrow$ )
4. For each pair  $(i, j)$ , add a directed arc  $x_i \leftarrow n_j$  if  $r_i(n_j(t))$
5. Remove reconstruction arcs / single nodes (**subgraph separation**)
6. For each subgraph/subset (strongly connected nodes)
  - i. Add reconstruction arcs with end nodes in the subgraph (+ starting nodes)
  - ii. Label weakly connected nodes as interpolation nodes

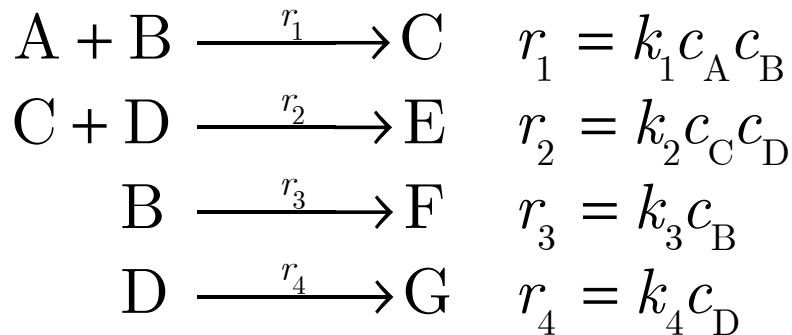
### SEPARATE MODEL IDENTIFICATION BETWEEN SUBSETS

- Rate expressions (rate parameters) corresponding to strongly connected extent nodes of each subset are **identified (estimated) simultaneously**
- Extents corresponding to interpolation nodes are interpolated from their measurements or simulated from models identified in previous subsets

# SIMULATED EXAMPLE

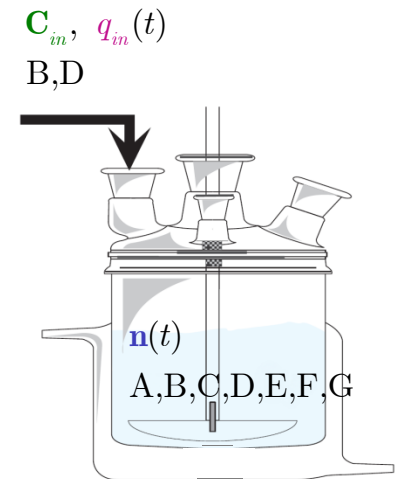
## Reaction system and operating conditions

- Reaction scheme



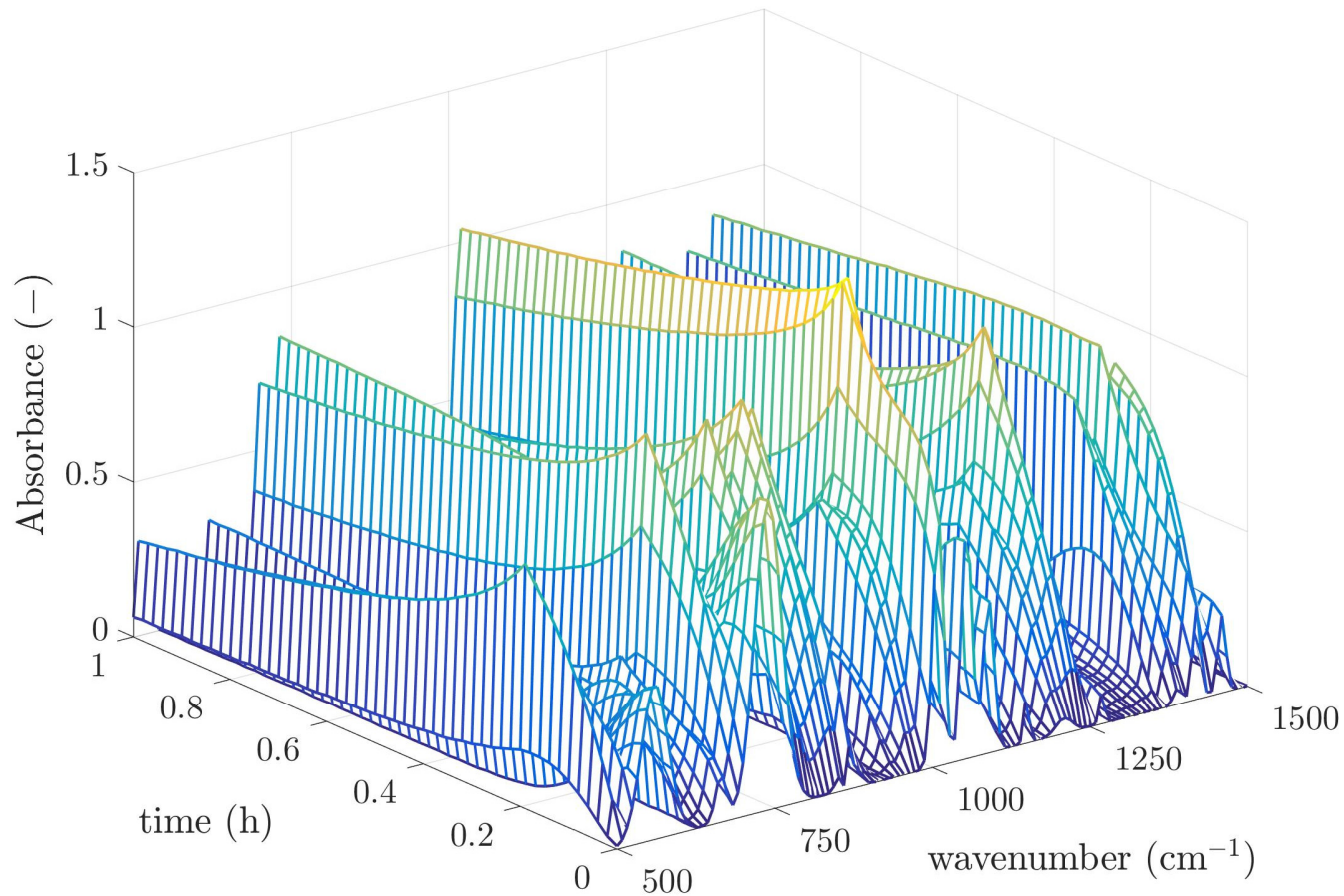
- Experimental conditions

- Species A is initially present (0.1 mol in 1 L)
- Species B (2 mol L<sup>-1</sup>) and D (1.5 mol L<sup>-1</sup>) are dosed at a flowrate  $q_{in}$  of 0.5 L h<sup>-1</sup> for 12 min
- All species absorb except species F and G
- The absorbance (500 and 1500 cm<sup>-1</sup>) is measured for 60 min



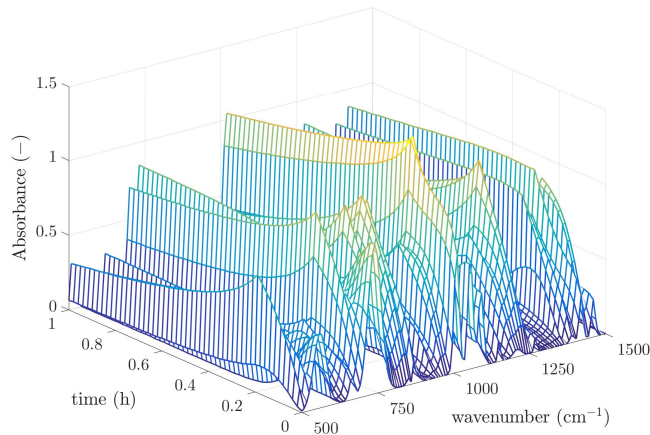
# SIMULATED EXAMPLE

## Multivariate spectroscopic measurements

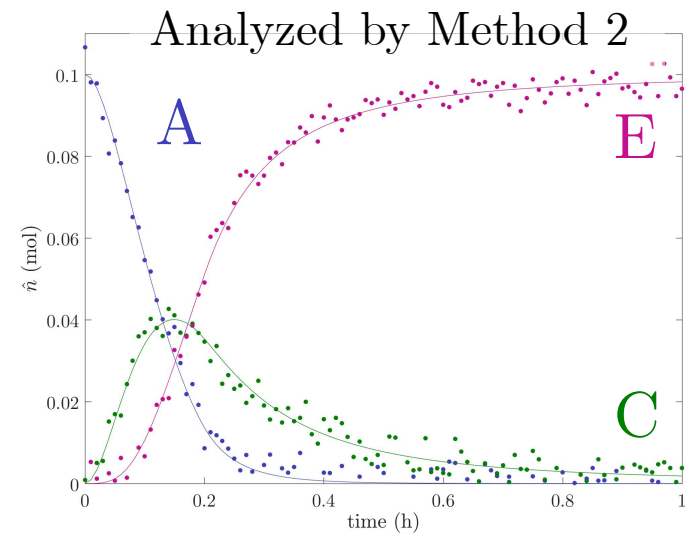
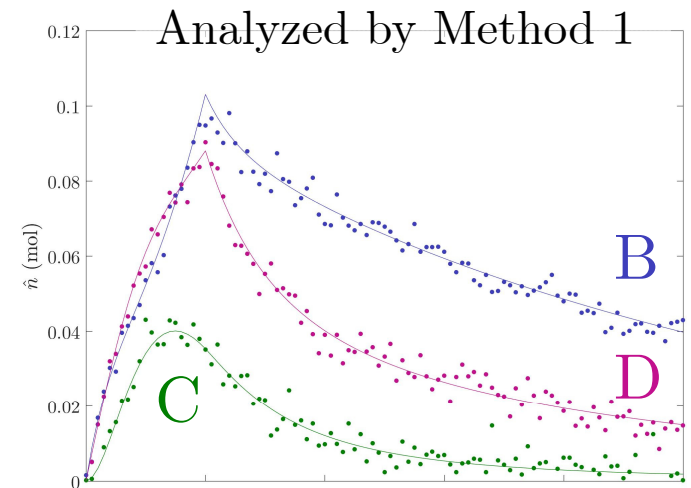


# SIMULATED EXAMPLE

## Predicted concentrations



PCR model





# SIMULATED EXAMPLE

## 1. Dynamic modeling / Static reconstruction

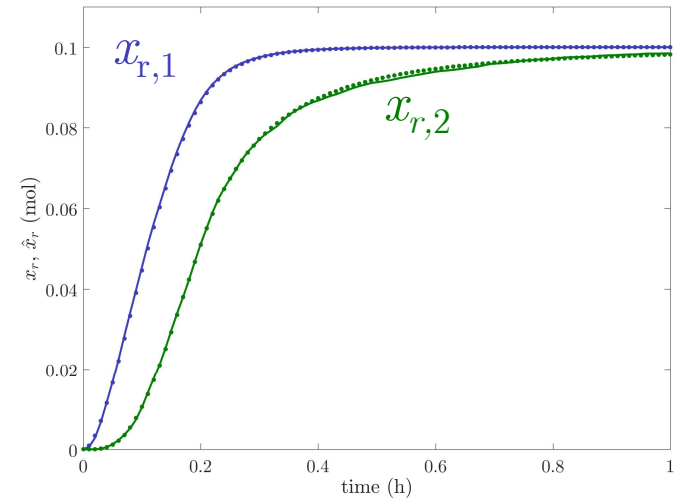
### 1A. SIMULTANEOUS IDENTIFICATION

of  $R_1 = 2$  reactions ( $x_{r,1}$ ,  $x_{r,2}$ )

$$\hat{k}_1 = 206 \pm 4 [194, 217] (99.7\%),$$

$$\hat{k}_2 = 149.5 \pm 0.4 [148.2, 150.8] (99.7\%),$$

$$(k_{1,true} = 200, k_{2,true} = 150)$$



# SIMULATED EXAMPLE

## 1. Dynamic modeling / Static reconstruction

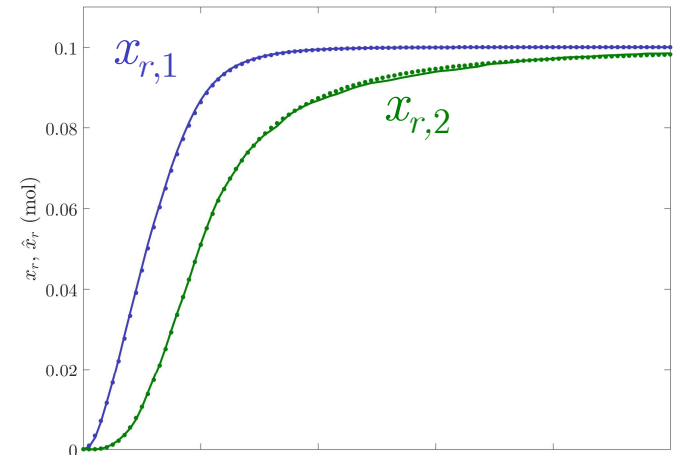
### 1A. SIMULTANEOUS IDENTIFICATION

of  $R_1 = 2$  reactions ( $x_{r,1}, x_{r,2}$ )

$$\hat{k}_1 = 206 \pm 4 [194, 217] \text{ (99.7\%)},$$

$$\hat{k}_2 = 149.5 \pm 0.4 [148.2, 150.8] \text{ (99.7\%)},$$

$$(k_{1,true} = 200, k_{2,true} = 150)$$



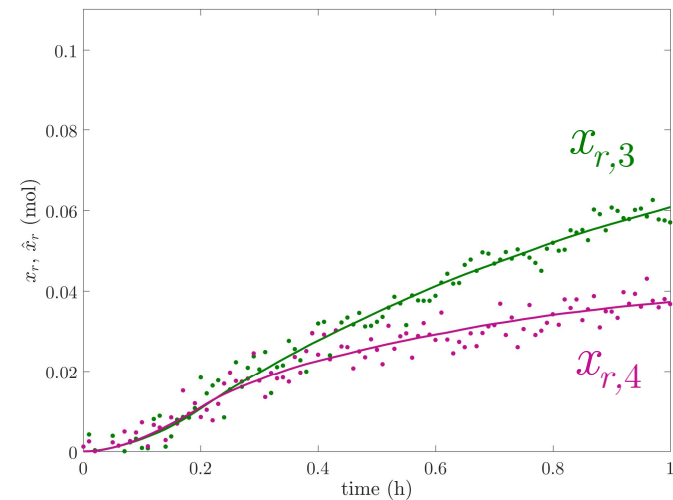
### 1B. INCREMENTAL IDENTIFICATION

of the  $R_2 = 2$  reactions ( $x_{r,3}, x_{r,4}$ )

$$\hat{k}_3 = 1.02 \pm 0.01 [1.00, 1.04] \text{ (99.7\%)},$$

$$\hat{k}_4 = 1.02 \pm 0.01 [0.99, 1.04] \text{ (99.7\%)},$$

$$(k_{3,true} = 1.00, k_{4,true} = 1.00)$$



# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems

Matrix of stoichiometry  $\mathbf{N}$

$$\mathbf{N} = \begin{bmatrix} -1 & -1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 1 \end{bmatrix}$$

Stoichiometric matrix of measured species  $\mathbf{N}_a$  (A, C, E)

$$\mathbf{N}_a = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

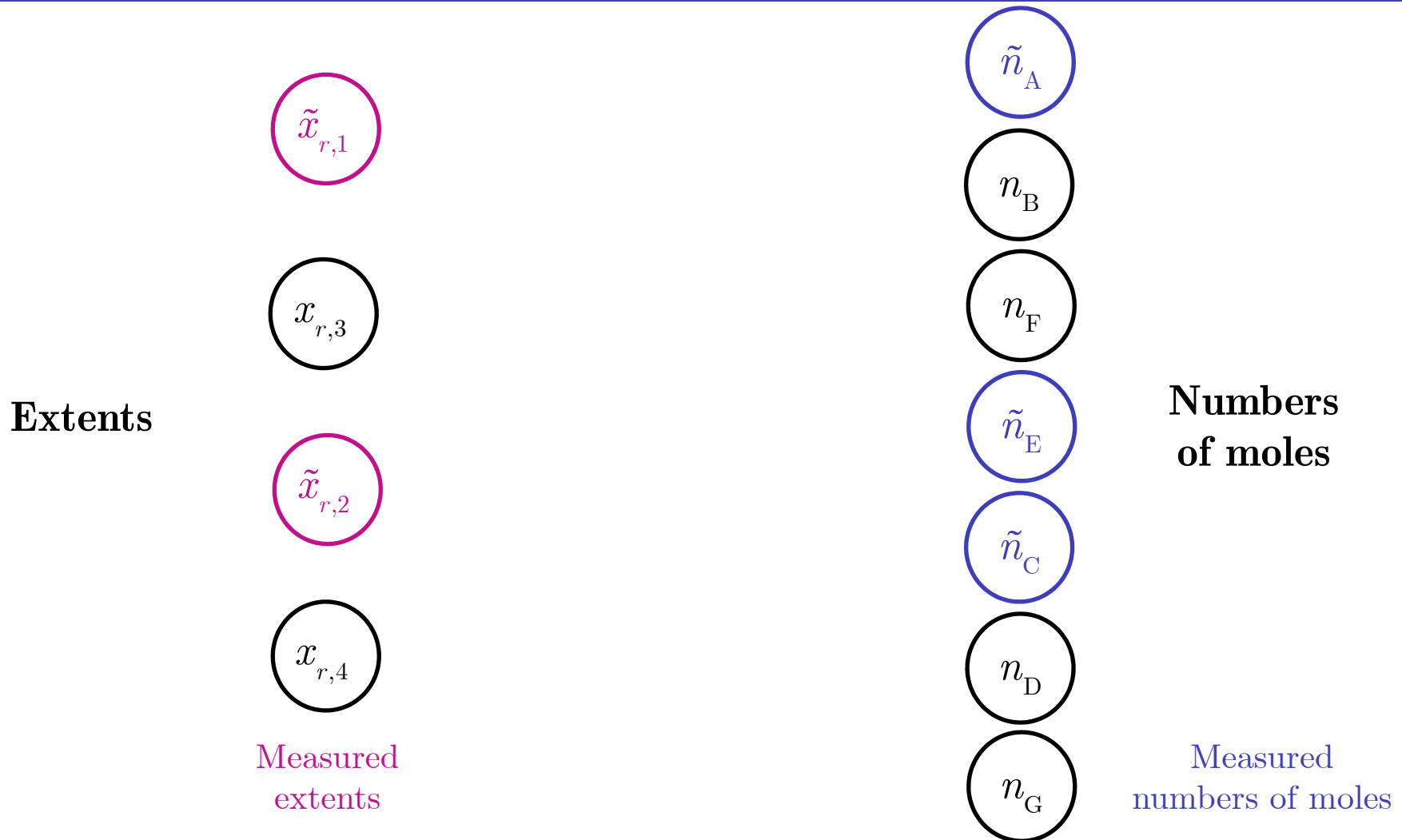
Construction of the matrix  $\mathbf{S}$

$$\mathbf{N}_a^T \xrightarrow[\text{remove rows of 0's}]{\text{rref}} \mathbf{S} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 \end{bmatrix} \quad \text{s.t. } \mathbf{N}_a^T (\mathbf{S}^T \mathbf{S}) = \mathbf{N}_a^T \quad \text{and } \mathbf{S}^T \mathbf{S} \neq \mathbf{I}_R$$

$\Rightarrow x_{r,1}$  and  $x_{r,2}$  are measured!

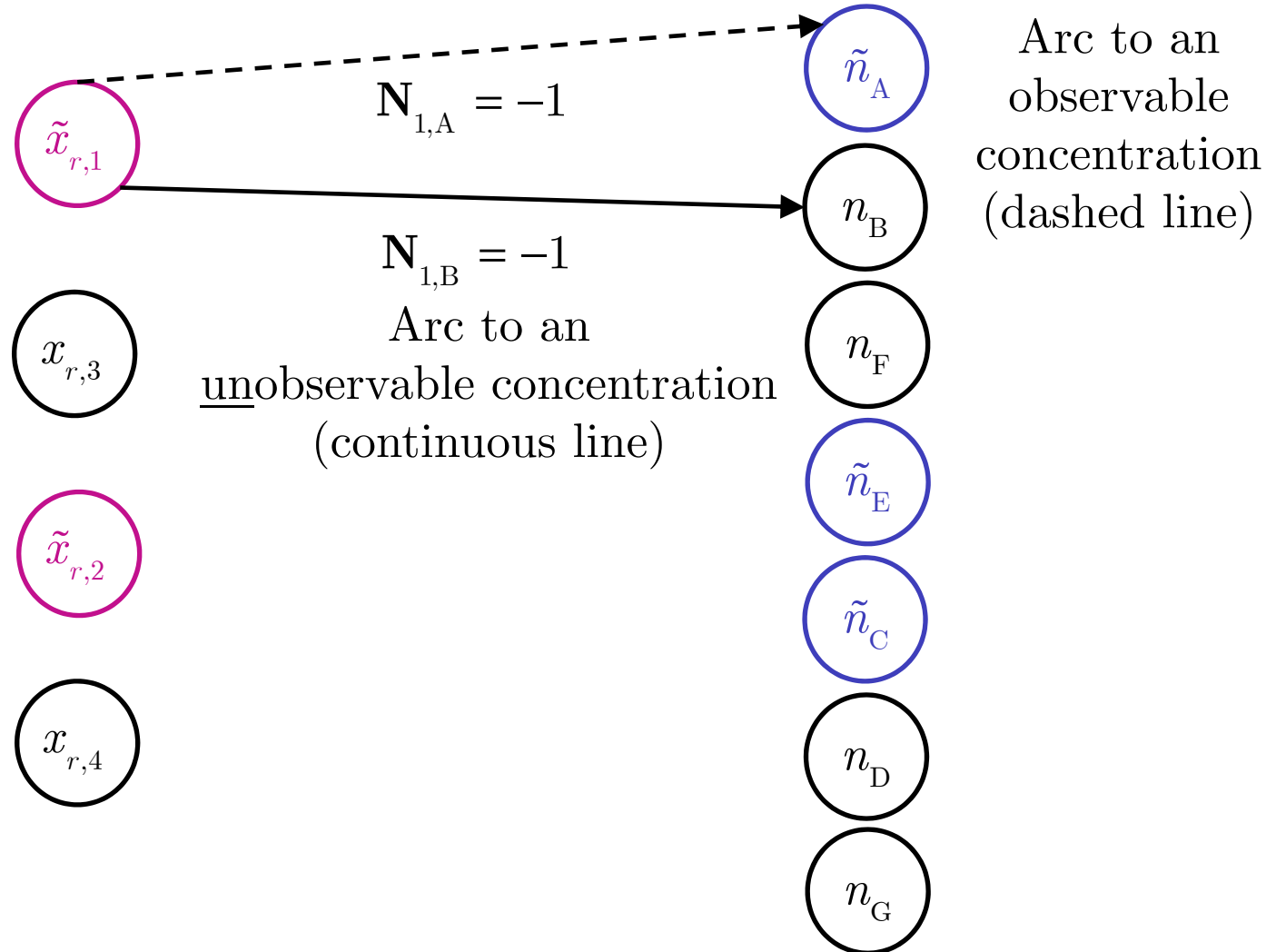
# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems



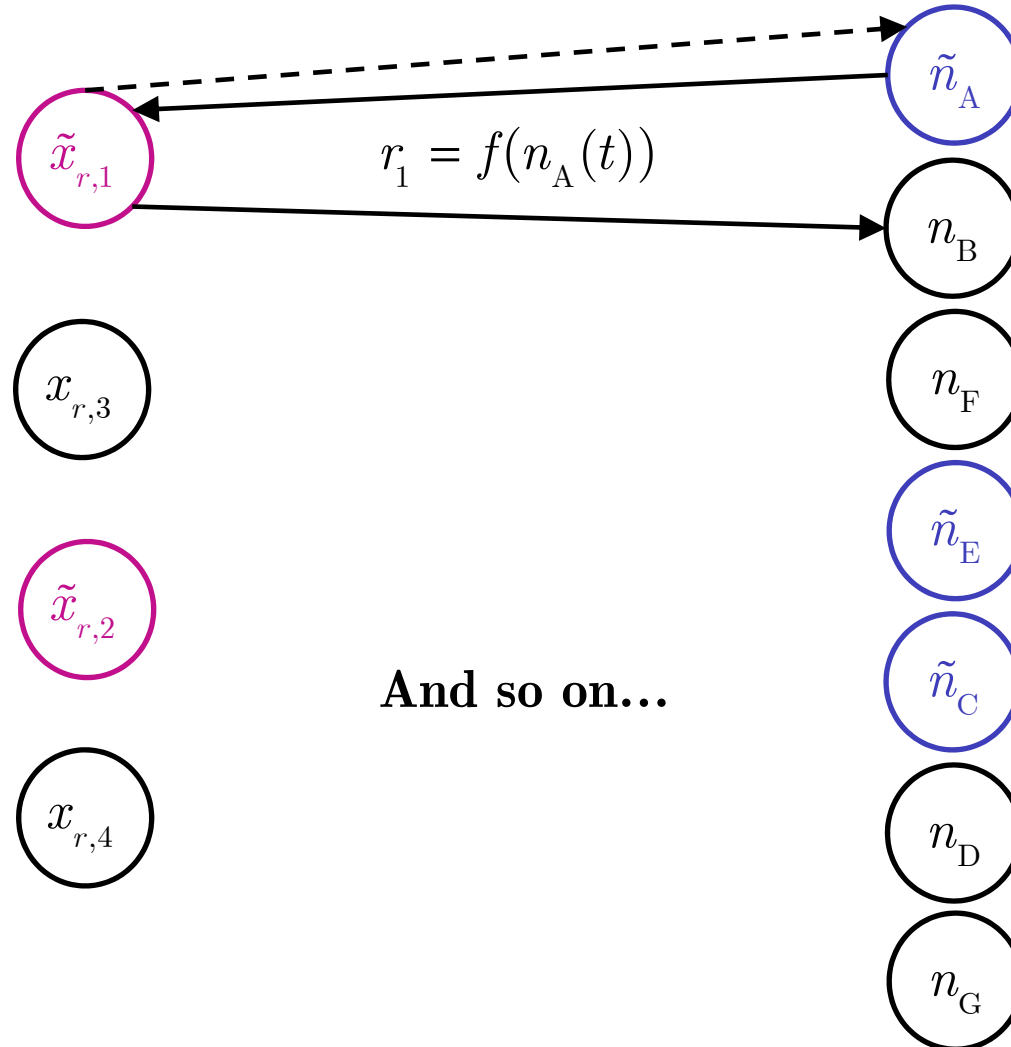
# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems



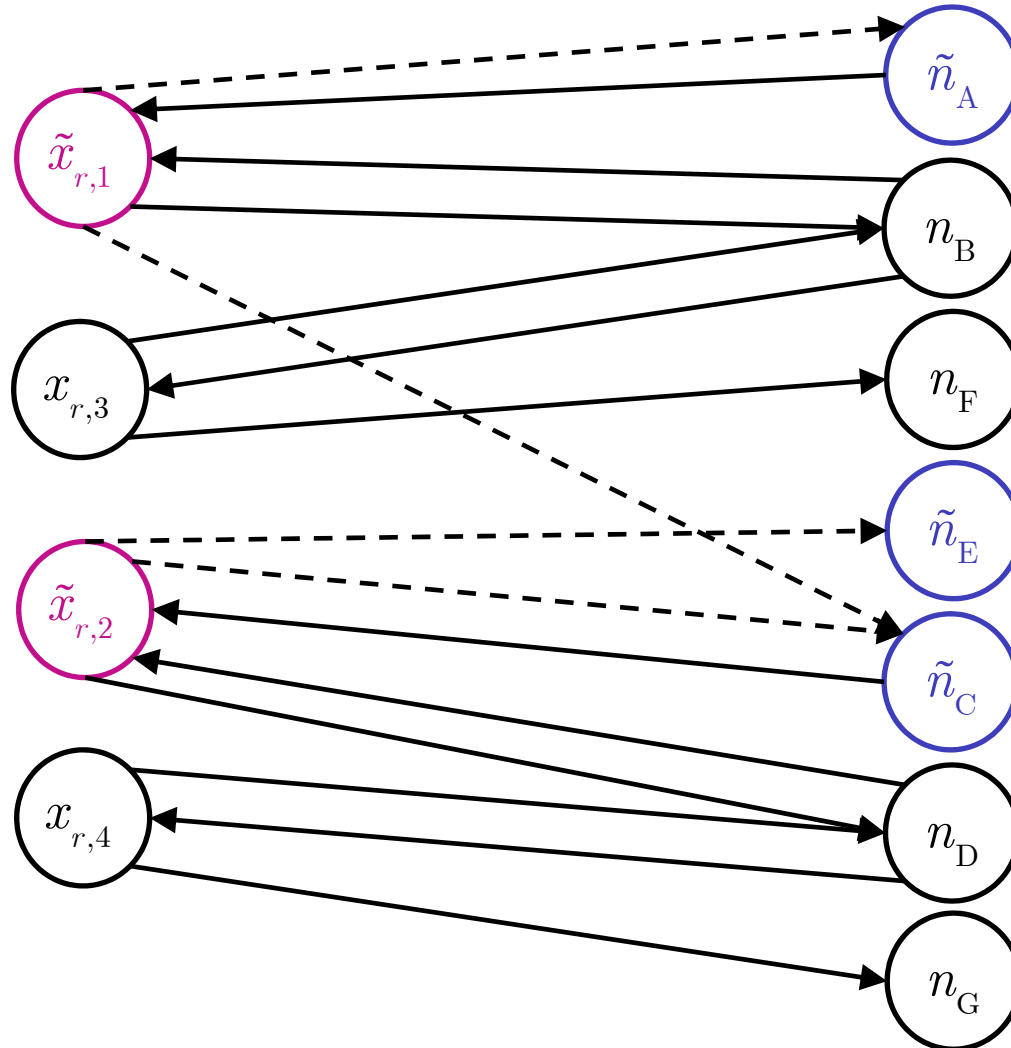
# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems



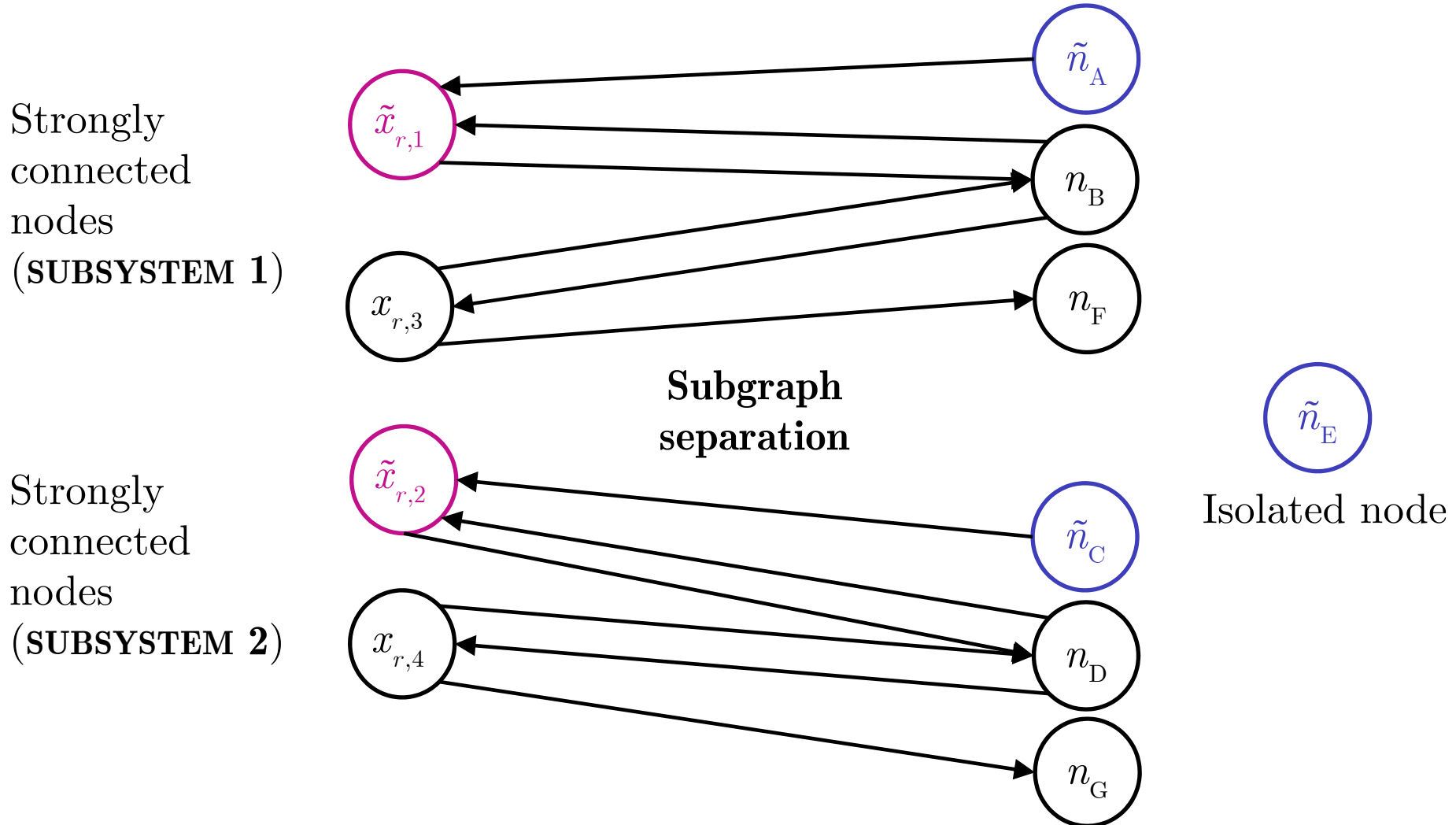
# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems



# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems

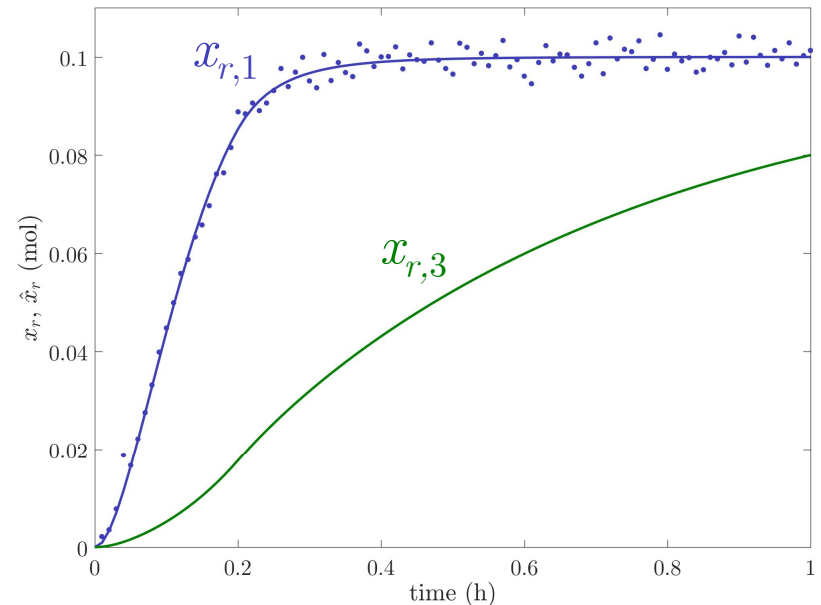
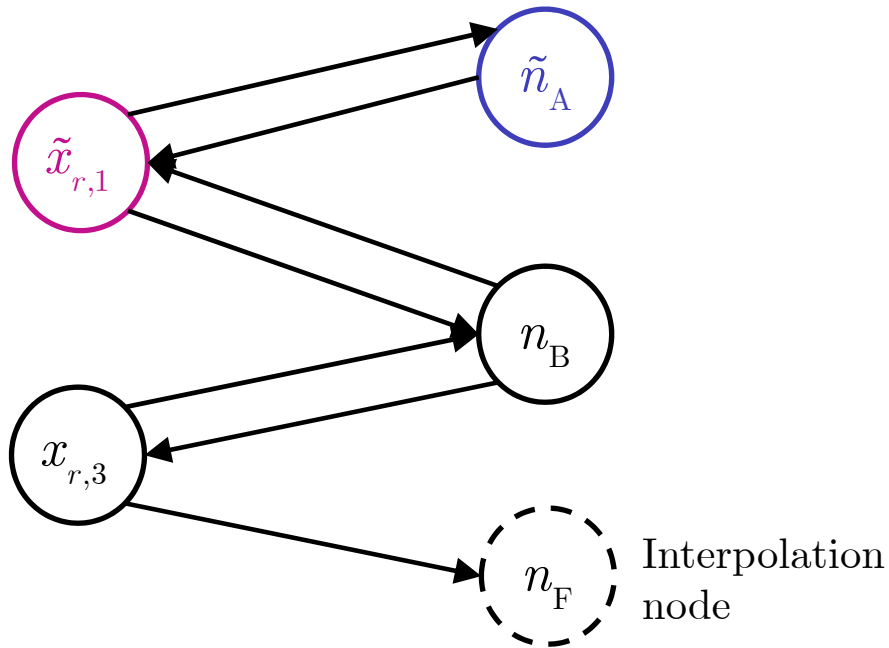




# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems

### REACTION SUBSYSTEM 1

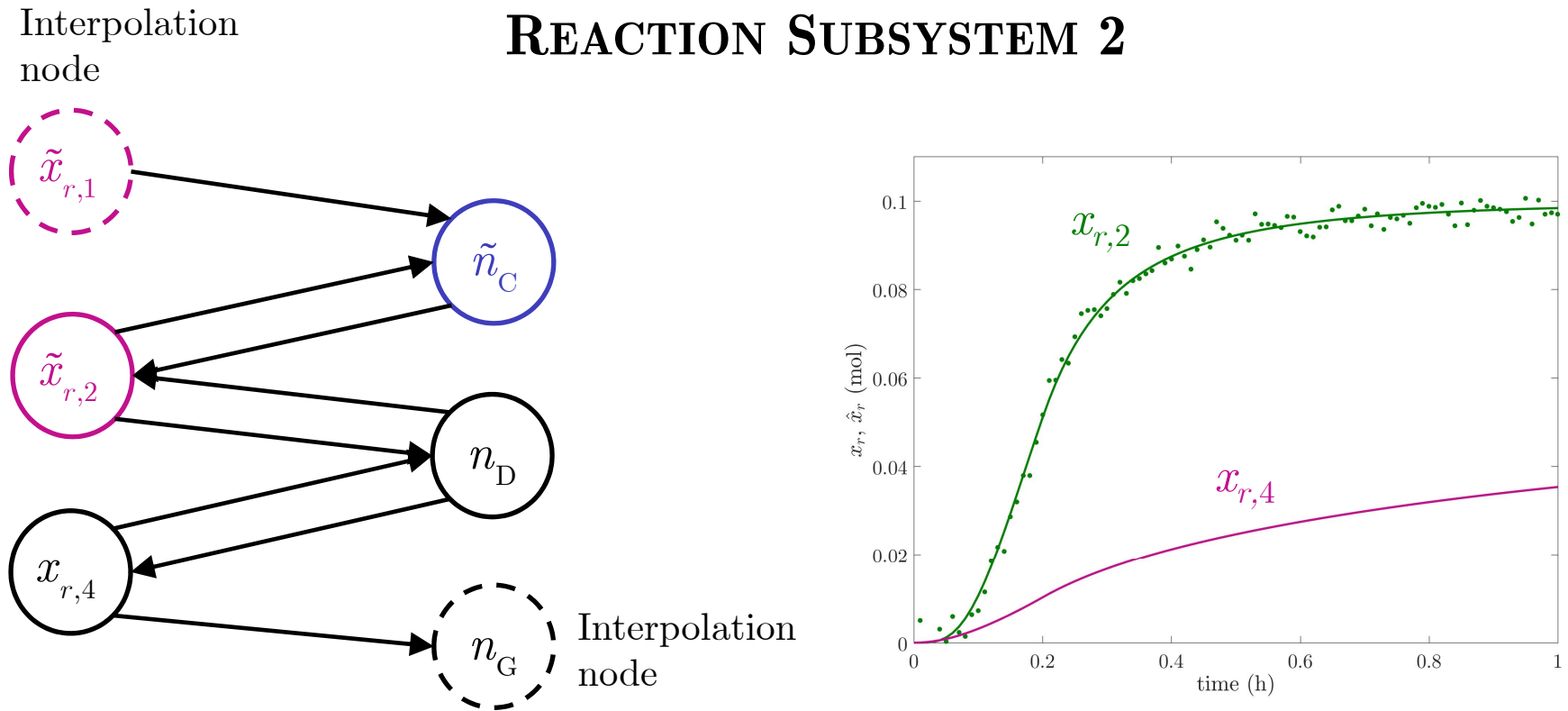


$$\hat{k}_1 = 200 \pm 5 [185, 214] (99.7\%), k_{1,true} = 200$$

$$\hat{k}_3 = 1.7 \pm 0.3 [0.9, 2.5] (99.7\%), k_{3,true} = 1$$

# SIMULATED EXAMPLE

## 2. Simultaneous identification of subsystems



$$\hat{k}_2 = 153 \pm 3 [143, 163] (99.7\%), k_{2,true} = 150$$

$$\hat{k}_4 = 0.9 \pm 0.1 [0.7, 1.2] (99.7\%), k_{4,true} = 1$$

# CONCLUSION AND PERSPECTIVES

Incremental kinetic modeling via a reduced spectroscopic calibration model  $S_a < R$  is possible in two ways:

- Method 1** Modeling simultaneously  $(R - S_a)$  reaction extents, and modeling incrementally the remaining extents;
- Method 2** Expressing the effects of the  $R$  reactions by means of  $S_a < R$  extents, and identifying the subsets of reactions whose rate expressions can be identified separately (between subsets)

## OPEN QUESTIONS

- Method 1** - In which conditions does it allow an incremental modeling?
- Method 2** - In which conditions does it allow subgraph separation?  
- Use of empirical extents (linear combinations of extents)?

# THANK YOU FOR YOUR ATTENTION

## ANNOUNCEMENT

In July 2017, **Prof. D. Bonvin** will retire and the **Laboratoire d'Automatique** of the EPFL will close its doors!

### References

- Bhatt N., Amrhein M., Bonvin D., Incremental identification of reaction and mass-transfer kinetics using the concept of extents, *Ind. Eng. Chem. Res.* 50 (2011) 12960
- Billeter J., Srinivasan S., Bonvin D., Extent-based kinetic identification using spectroscopic measurements and multivariate calibration, *Anal. Chim. Acta.* 767 (2013) 21
- Rodrigues D., Srinivasan S., Billeter J., Bonvin D., Variant and invariant states for chemical reaction systems, *Comp. Chem. Eng.* 73 (2015) 23
- Masic A., Billeter J., Bonvin D., Villez K., Extent computation under rank-deficient conditions, *IFAC World Congress 2017* (available on <https://infoscience.epfl.ch/record/224435>)
- Billeter J., Villez K., Bonvin D., Extent-based model identification using a reduced set of measurements, *in preparation*