UNIVERSITY of WASHINGTON

Forecasting Perovskite Photovoltaic Device Performance.
Predictive Machine Learning from small Scientific Datasets

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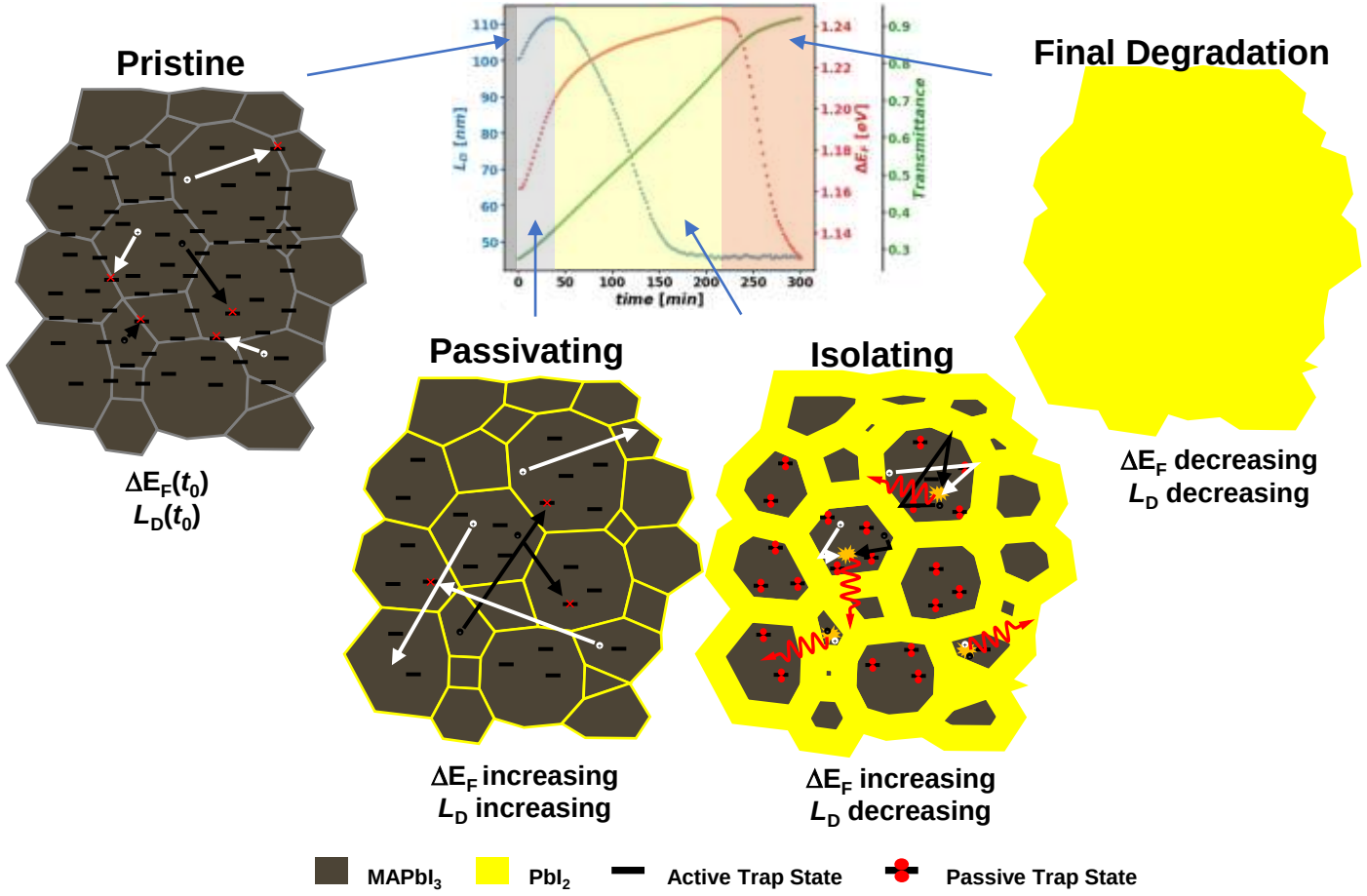
Solar Applications of Artificial Intelligence and Machine Learning

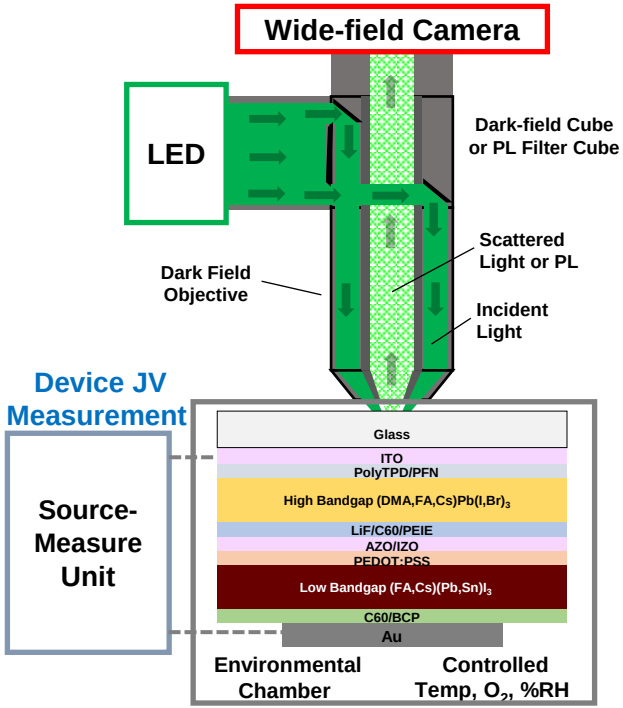
October 31-November 1, 2023

Evolution of Optoelectronic Properties During Degradation



Stoddard, Dunlap-Shohl, Qiao, Meng, Kau, and Hillhouse. *ACS Energy Lett.*, **2020,** *3*, 946-954

Forecasting Perovskite Photovoltaic Device Performance Using Dark-Field Imaging and Machine Learning



Goal Develop forecasting models for device PCE T80

- That account for device-to-device variation

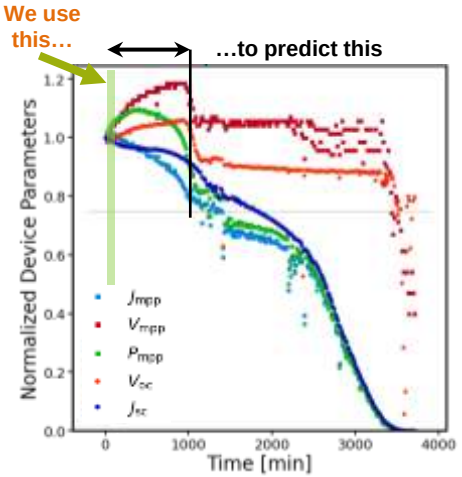
ML model inputs

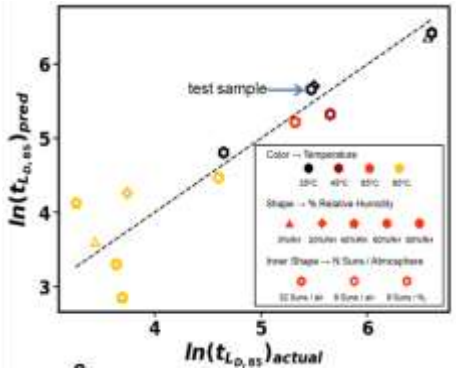
- time-series data of dark-field (DF) optical microscopy, summaries of wide-field photoluminescence (PL), current-voltage (JV) measurements
- all collected in-situ during degradation over a broad range of temperatures, relative humidity, oxygen, illumination intensity
- all **early time features**

Hierarchical ML learn inputs to forecasting model

- E.g. absorber material and single-junction sub-cell degradation rates from unencapsulated devices

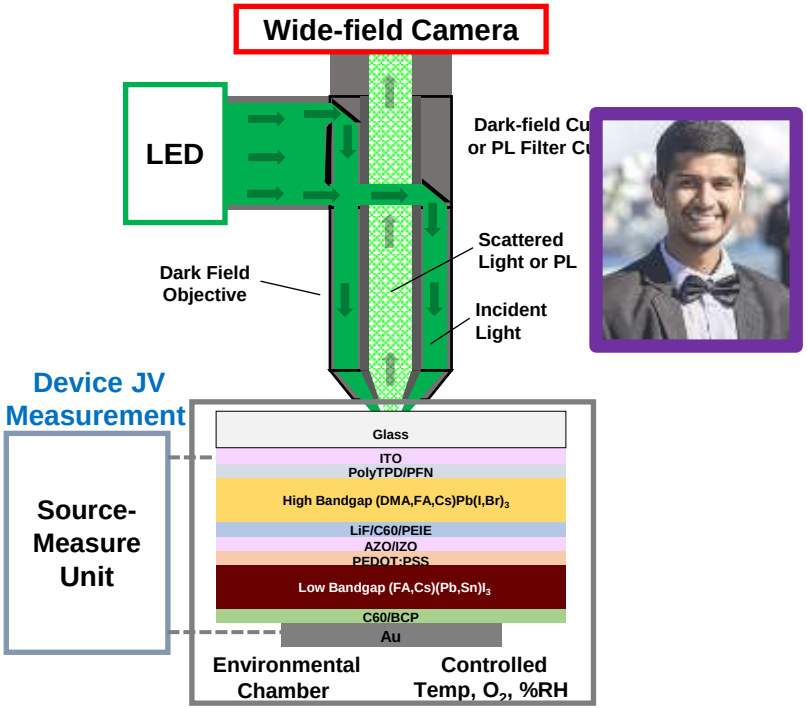
Validation with state-of-the art statistical methods





Award # DE-EE0009351 PI Hillhouse, CoPI Beck, Meila

Forecasting Perovskite Photovoltaic Device Performance Using Dark-Field Imaging and Machine Learning



PI Hillhouse (UW Chemical Engineering)

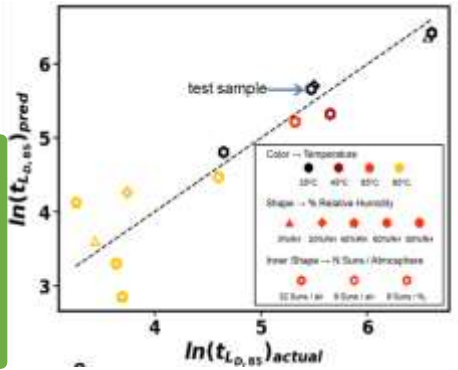
Hillhouse Lab Yuhuan Meng, **Preetham Sunkari**, Spencer Cira and former members

Co PI Beck (UW Chemical Engineering) big data pipeline

Co PI Meila (UW Statistics) **Machine Learning/Statistical Learning**

NDSEG Fellow (UW Statistics) **Alex Kokot** and former members

Tom Lejtens (Swift Solar) Device fabrication



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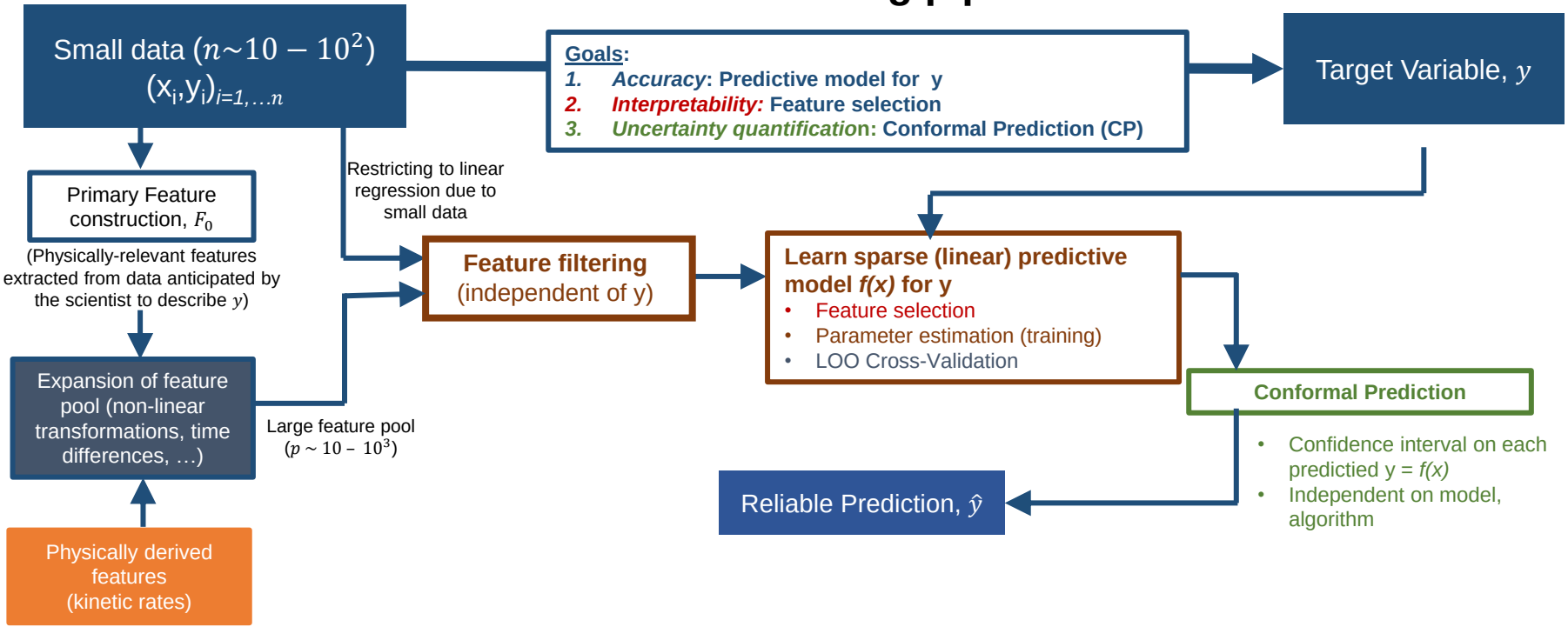
Prediction modeling pipeline



Challenges of small data

- **Where** experiment expensive: $$$, time, human effort, expertise
- **Statistics** and **computation** must make up for data paucity
- **Benefits** some computations possible that are intractable for large data

Training + feature selection with small data

1. *Algorithms* Lasso, best-subset selection, OMP, knockoffs
2. *Prediction* accuracy *evaluation:* Training errors, in-sample errors like AIC and BIC, and extra-sample test errors using leave-one-out cross validation.
3. .

Small data challenges and benefits

- Why **small data** setting?
  - Small data = (statistical) asymptotics do not hold
  - Domain knowledge needed to constrain the model

In degradation experiments n ~ 40-100 experiments, p ~ 100-300 features

-- Experiment expensive: $$$, **time**, human effort, expertise

- **Statistics** and **computation** must make up for data paucity

- Constraints from small data
  - Only *linear* models
  - And only *sparse* models s features used out of p
  - Informational limit $n \propto s \log_2 p$

Degrees of freedom (dof)[1]

Example $n = 35,\ p = 128 = 27$

- for $s = 1$: $n / \log_2 p = 5$ data points/dof
- For $s = 2$: $n / s \log_2 p = 2.5$ data points/dof

[1] D. L. Donoho, "Compressed sensing," in *IEEE Transactions on Information Theory*, vol. 52, no. 4, pp. 1289-1306, April 2006, doi: 10.1109/TIT.2006.871582.

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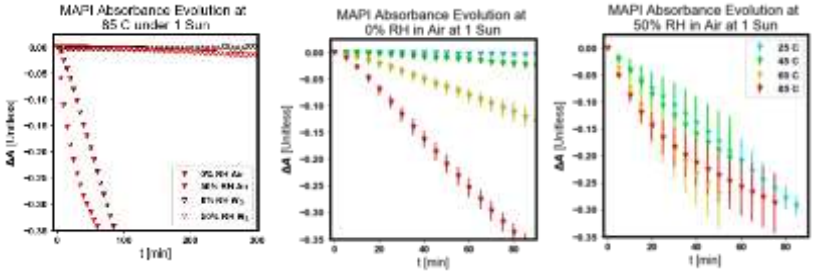
- Constraints from small data
  - Only *linear* models
  - And only *sparse* models s features used out of p
  - Informational limit $n \propto s \log_2 p$
  - Must **filter features** before training model
    - E.g remove redundant features
    - + transform features to conform with linearity
  - Can leverage **independent experiments** to *construct physically inspired features*

Physiochemical Inspired Feature: Kinetic Rate Equation for $MAPbI_3$ Degradation

The rate of disappearance of perovskite can be quantified from changes in the above bandgap absorbance using Beer's Law:

$$r = -\frac{1}{W}\frac{dN}{dt} = -\frac{\rho}{M \cdot log_{10}(e) \cdot \alpha_0}\frac{d\Delta A}{dt}$$

Absorbance of $MAPbI_3$ films measured in-situ over broad range of conditions (41 unique environmental conditions)

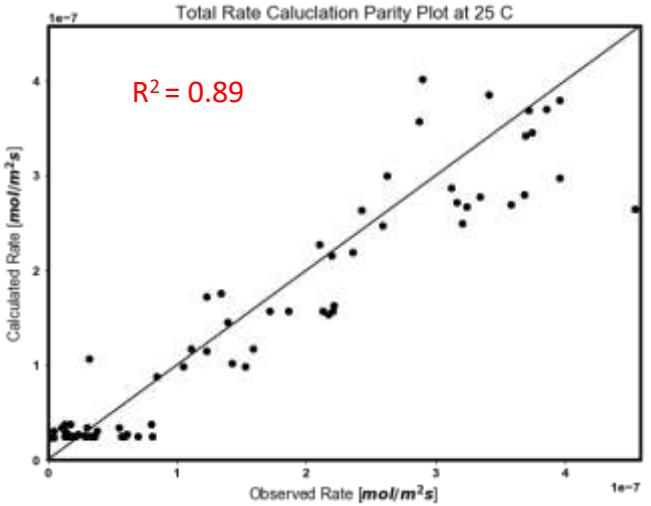


Degradation Conditions	25 °C with 1 Sun [mol/(m²·s)]	85 °C with 1 Sun [mol/(m²·s)]
Heat Only (0% O_2, 0% RH)	less than 10^{-10}	less than 10^{-10}
Humid N_2 (0% O_2, 50% RH)	1×10^{-9}	3×10^{-9}
Dry Air (21% O_2, 0% RH)	4×10^{-9}	2×10^{-7}
Humid Air (21% O_2, 50% RH)	2×10^{-7}	4×10^{-7}

Degradation rate at 25 °C in humid air is ~2 orders of magnitude faster than the ***sum*** of all other processes.

Rate equation derived from hypothesized elementary steps of the reaction with an assumption of a rate determining step

$$r = -k\frac{P_{H_2O}P_{O_2}n}{\left(1 + K_2P_{O_2}(1 + K_4n)\right)^2}$$



T.D. Siegler, W.A. Dunlap-Shohl, Y. Meng, W.F. Kau, P.P. Sunkari, C.E. Tsai, Z.J. Armstrong & H.W. Hillhouse, "Water-Accelerated Photo-oxidation of $CH_3NH_3PbI_3$ Perovskite: Mechanism, rate orders, and rate constants," **(2022)**

Small data challenges and benefits: algorithms

- Constraints from small data
  - Only *linear* models
  - And only *sparse* models s features used out of p
  - Informational limit $n \propto s \log_2 p$
- Benefits
  - can exploit computational methods that are prohibitive for larger data (e.g. exhaustive search)

- ML Algorithms incorporating feature selection (Many!)
  - Lasso (l1 regularization) -- convex optimization
  - Orthogonal Matching Pursuit (OMP) -- greedy
  - Best subset selection -- exhaustive search over all feature sets of size s
  - Knock-offs (Lasso + control of False Discovery Rate)

Sparse Linear Models

Most commonly-used sparse linear models use penalized versions of the ordinary least-squares (OLS) cost function.

OLS cost function, $\mathcal{L}_{OLS} = \sum_{i=1}^{N}\left(y_i - \sum_{j=0}^{p}\beta_j X_j\right)^2$

l_0 (a.k.a ***best-subset*** regression)

$$\boldsymbol{\beta}^* = \min_{\boldsymbol{\beta}=\{\beta_j:\, j=1,2,\ldots,p\}} \mathcal{L}_{OLS}$$

such that $\|\boldsymbol{\beta}\|_0 = \sum_{j=1}^{p} 1\{\beta_j \neq 0\} \leq m$

- Generates a sparse coefficient array, $\boldsymbol{\beta}^*$ corresponding to a feature subset with size, s that corresponds to the lowest error.
- Subset-size, s is the only tunable parameter and is easy to interpret.
- Fails to perform well when the noise levels are large [1][2].

Exhaustive search over all subsets

l_1 (a.k.a ***lasso*** regression)

$$\boldsymbol{\beta}^* = \min_{\boldsymbol{\beta}=\{\beta_j:\, j=1,2,\ldots,p\}} \mathcal{L}_{OLS} + \lambda_1\|\boldsymbol{\beta}\|_1$$

where $\|\boldsymbol{\beta}\|_1 = \sum_{j=1}^{p}|\beta_j|$

- Generates a sparse coefficient array, $\boldsymbol{\beta}^*$
- The coefficients of the selected features are "shriunk" such that the error is minimized [1]; Robust to high noise levels [1].
- Complex iterative hyper-parameter (λ_1) tuning is needed to obtain a feature subset with the desired size, s[1]; Less sparse compared to $\boldsymbol{l_0}$[2].

Automatic efficient search for all λ_1

$l_0 l_2$

$$\boldsymbol{\beta}^* = \min_{\boldsymbol{\beta}=\{\beta_j:\, j=1,2,\ldots,p\}} \mathcal{L}_{OLS} + \lambda_2\|\boldsymbol{\beta}\|_2$$

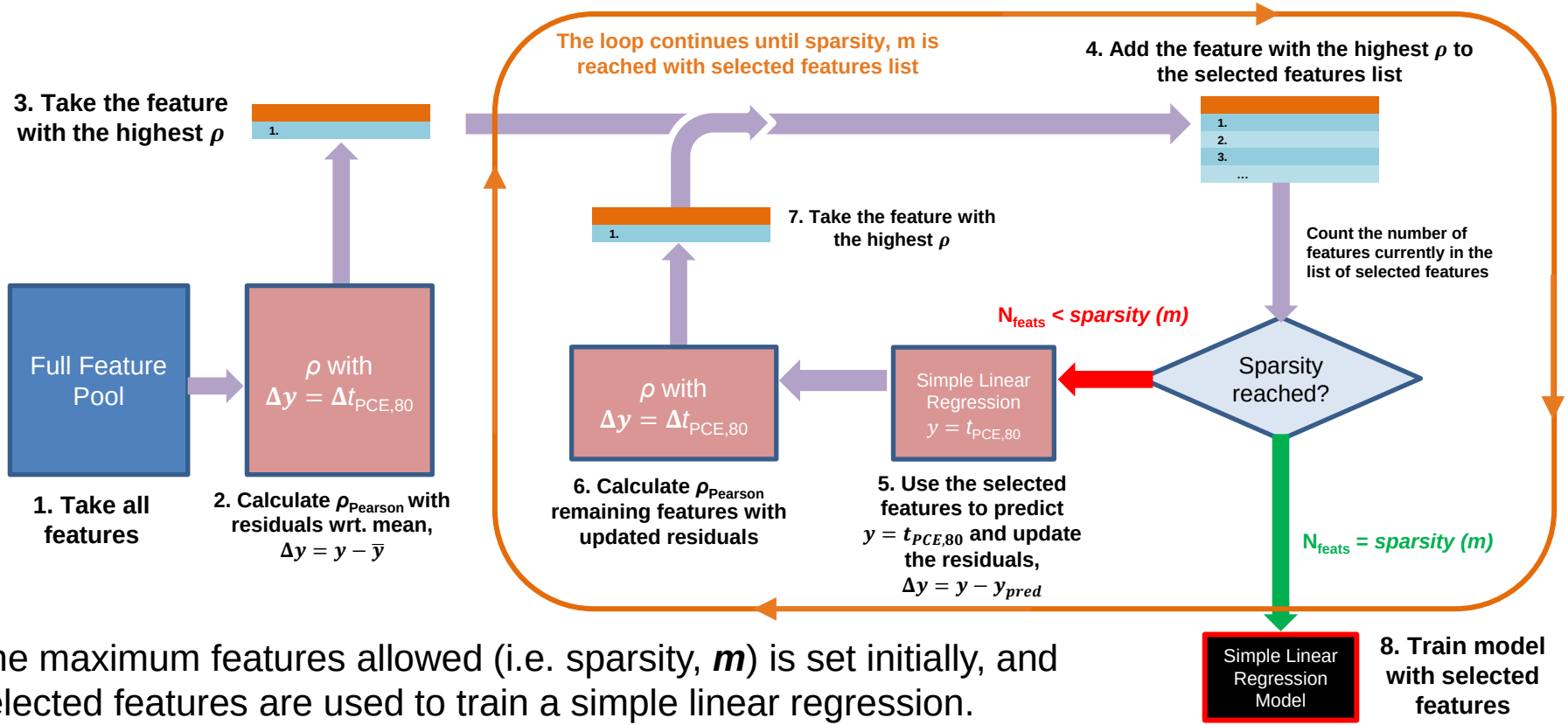
where $\|\boldsymbol{\beta}\|_2 = \sum_{j=1}^{p}\beta_j^2$ such that $\|\boldsymbol{\beta}\|_0 \leq m$

- Same as $\boldsymbol{l_0}$ with Ridge Regression
- The coefficients of the selected features are "shrinked" such that the error is minimized [2]; Robust to high noise levels [2] and preserves the sparsifying ability of the $\boldsymbol{l_0}$ method [2].
- Although setting s sets the resultant subset-size, tuning the hyper-parameter (λ_2) increases the runtimes.

[1] Hastie T., Tibshirani R., Tibshirani R. J., (2017) Extended Comparisons of Best Subset Selection, Forward Stepwise Selection, and the Lasso, arXiv: 1707.08692v2.
[2] Mazumder R., Radchenko P., Dedieu A. (2023) Subset Selection with Shrinkage: Sparse Linear Modeling When the SNR Is Low. Operations Research 71(1):129-147

Orthogonal Matching Pursuit (OMP)

A Greedy algorithm, which selects features sequentially based on the correlations with the updated residuals.



The maximum features allowed (i.e. sparsity, ***m***) is set initially, and selected features are used to train a simple linear regression.

Example: Prediction of $\log(1/t_{LD80})$ in $FA_{0.75}Cs_{0.25}(Pb_{0.5}Sn_{0.5})I_3$ thin films

Temperature

25 C 55 C

Relative humidity

0% RH

50% RH

Stress intensity

0 sun

1 sun

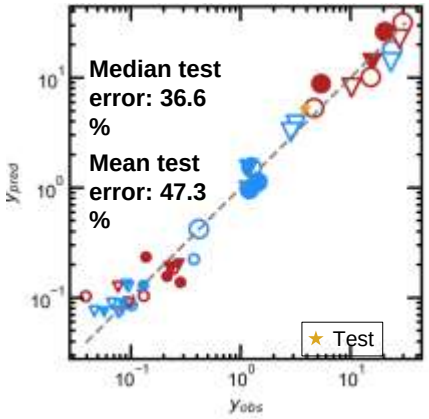
Oxygen %

~3% O_2

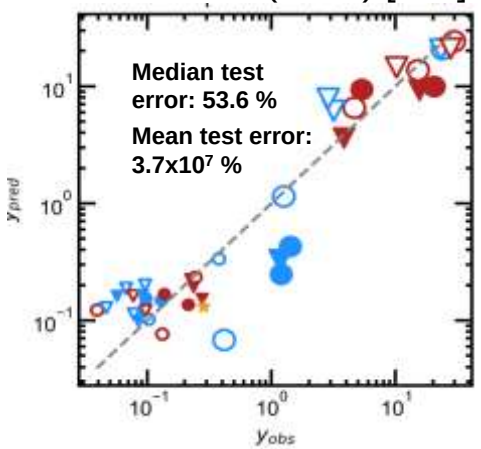
21% O_2

Median Model Predictionsl

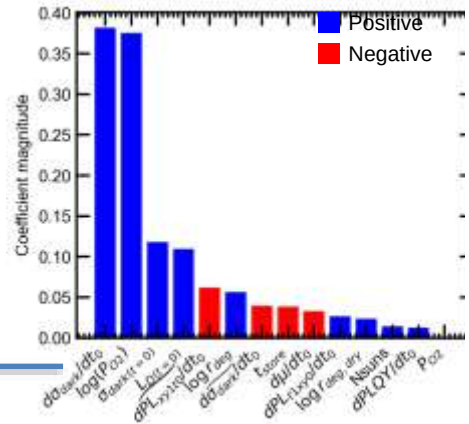
LASSO

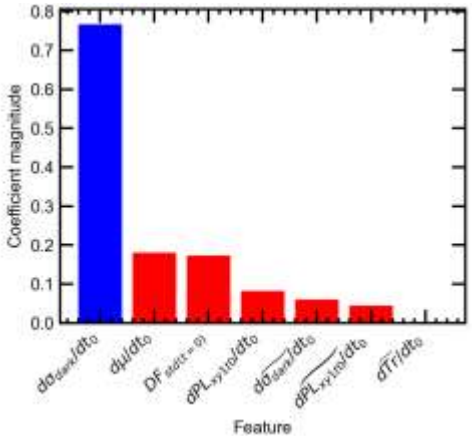


Orthogonal Matching Pursuit (OMP) [s=2]



Coefficients





n = 48 features

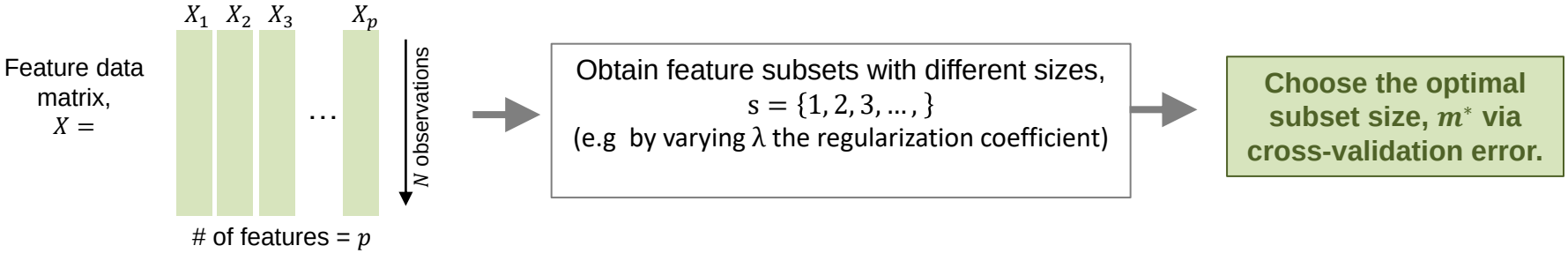
- experimental conditions
- Kinetic rate
- early-time measurements (based on L_D, PLQY, σ_{dark}, $\mathcal{T}$, DF,)

Selected features: $\frac{d\sigma_{dark}}{dt}$, $\log PO_2$, $\sigma_{dark}(t=0)$, $\log\ r$, ….

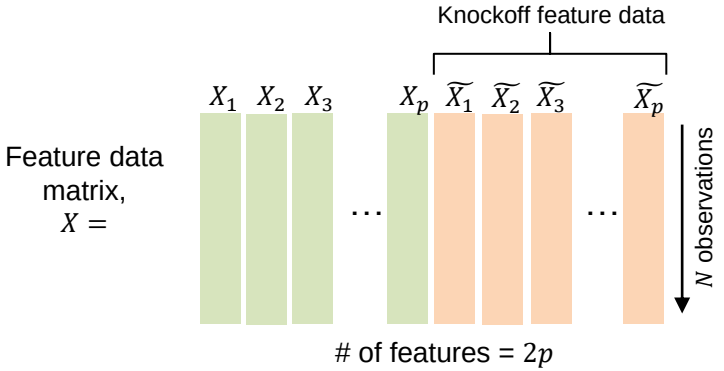
Knockoff Filter for the Sparse Linear Model

- By incorporating the *knockoff+ filter* into the sparse linear model training, we can obtain feature subsets with ***guaranteed false-discovery rates.***

Traditional feature selection via a sparse linear model (l_0, l_1, or l_0l_2):



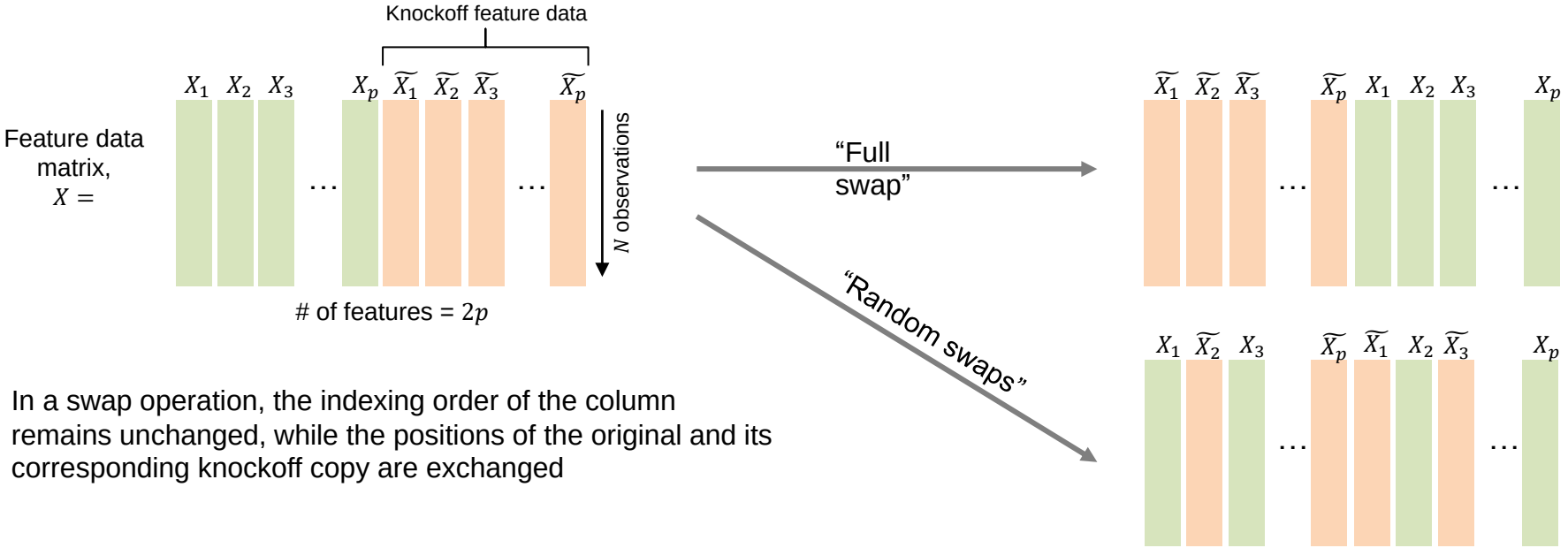
Feature selection via a sparse linear model (Lasso) augmented with a *knockoffs+* filter:



First, what are these knockoffs feature data?

Knockoff Feature Data

- Knockoff feature data are built without seeing the target variable data, y, such that the ***joint distribution of the feature matrix doesn't change*** with the swap operations as shown below [1].



In a swap operation, the indexing order of the column remains unchanged, while the positions of the original and its corresponding knockoff copy are exchanged

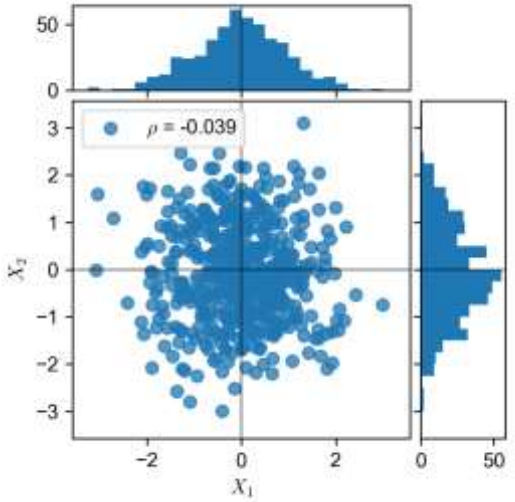
Knockoff feature data columns act as control group for the predictors that behaves in the same way as the original null variables but, unlike them, <u>lack any potential correlation with the target variable.</u>

[1] Barber R. F., Candes E. J., (2015) Controling the false-discovery rate via knockoffs. The Annals of Statistics Vol. 43, No. 5, 2055–2085

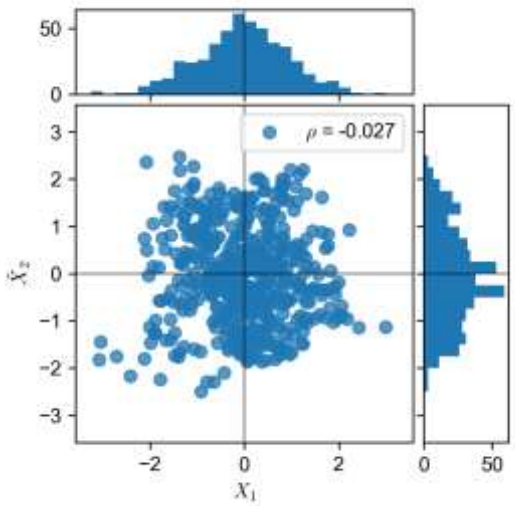
Knockoff Feature Data: Example

Consider the feature matrix, X (=$\{X_1, X_2, \}$) as shown below where $\rho(X_1, X_2)$ ~ 0.

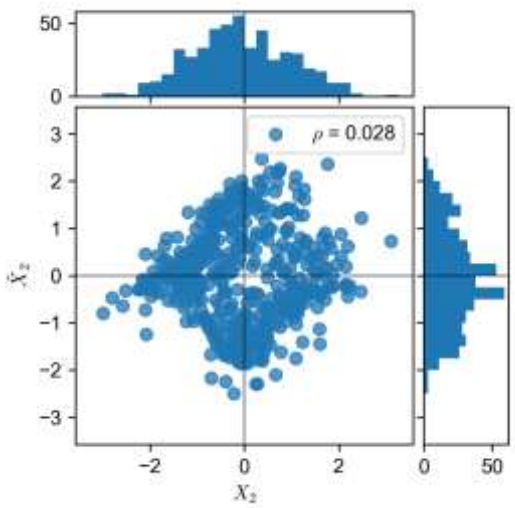
$P(X_1, X_2)$



$P(X_1, \widetilde{X_2})$



$P(X_2, \widetilde{X_2})$



Knockoff generator algorithm: Deep neural network [1]

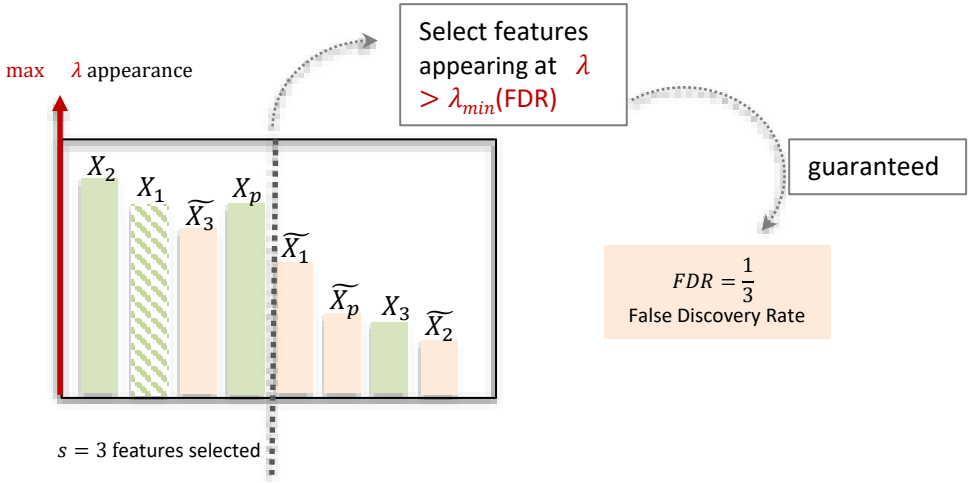
Using a knockoff algorithm to produce $\widetilde{X}_2$:

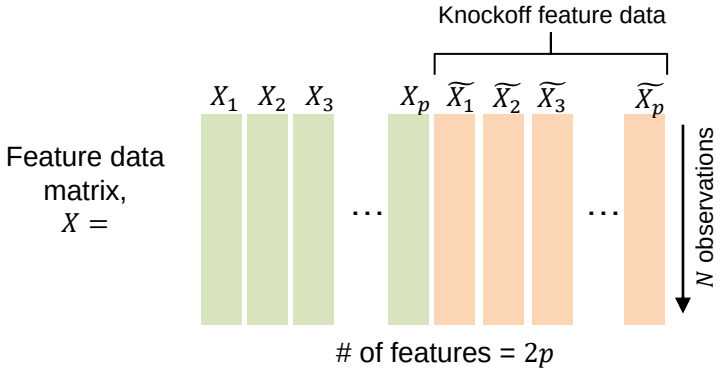
- **preserves the underlying joint distribution and correlation of X_1 and X_2**
- **while ensuring that the correlation between X_2 and $\widetilde{X}_2$ is as low as possible,**

thus, making $\widetilde{X}_2$ indistinguishable from X_2

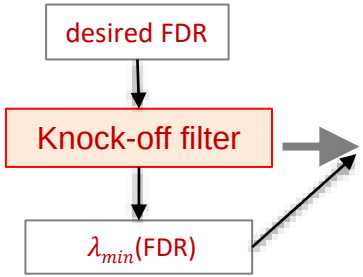
[1] Romano Y., Sesia M., Candes E. J., (2018) Deep Knockoffs, arXiv:1811.06687v1

Knock-off Filter for the Sparse Linear Model





Vary λ to obtain feature subsets with all sizes,s $= \{1, 2, 3, \ldots, 2p\}$



subset with desired nominal FDR.

By incorporating the *knockoff+ filter* into the sparse linear model training, we can obtain feature subsets with ***guaranteed false-discovery rates.***

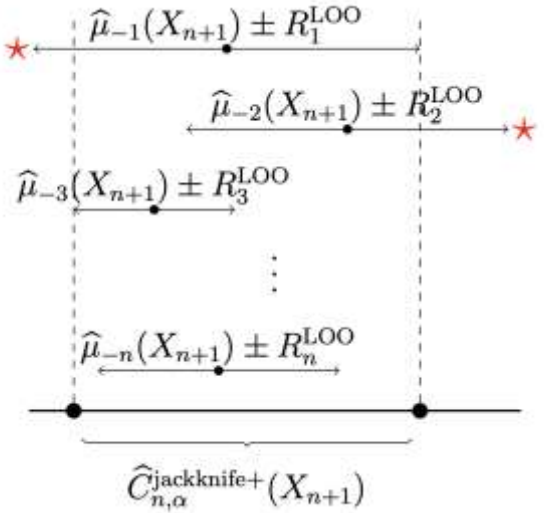
Uncertainty quantification by Conformal Prediction intervals

- **Confidence Interval (CI)**: a small [Y-, Y+] at high confidence level (90%) that *we believe* contains the truth

- **Conformal prediction (CP)**: recent powerful method to obtain confidence interval (CI) for a prediction
  - **CP Input:** training data (X_i, Y_i), prediction algorithm (e.g. LASSO), new input X, desired confidence level (e.g. 90%)
  - **CP Output**: prediction Y(X) and 90% CP interval [Y-, Y+] that contains Y(X)

- **Idea:** we want to guess the error of Y(X). Calculate the leave-one-out errors for the n data points $X_1 \ldots X_n$ for which $Y_1 \ldots Y_n$ are known. This gives a *distribution of the errors* that we can use.

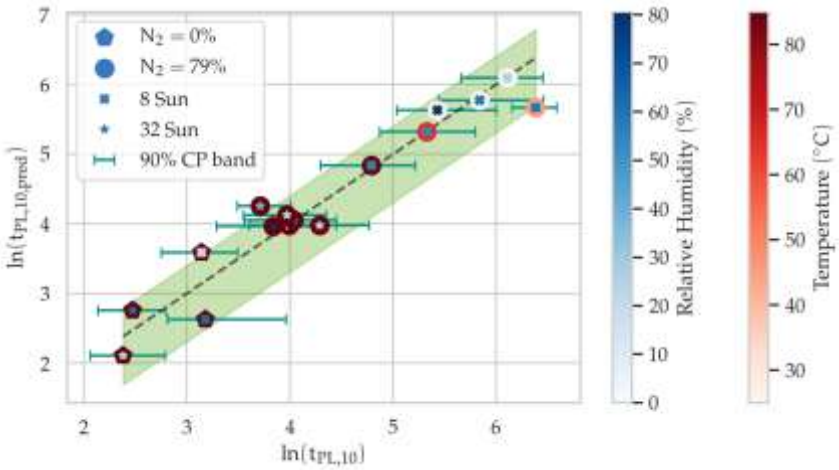
- Methods before CP
  - Classical Confidence Interval: depends on model used being correct
  - Bootstrap, Jackknife (resampling based methods): independent of model, but no proof of correctness
- With CP (here Jackknife+ algorithm [2])
  - The interval is correct no matter what data/model used
  - Requires re-training the model multiple times
  - Fast developing area of statistics

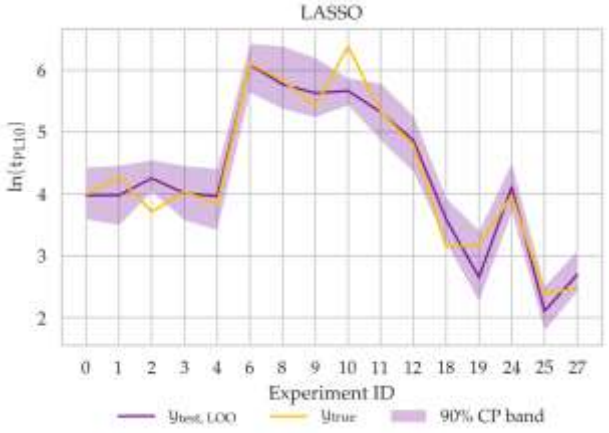


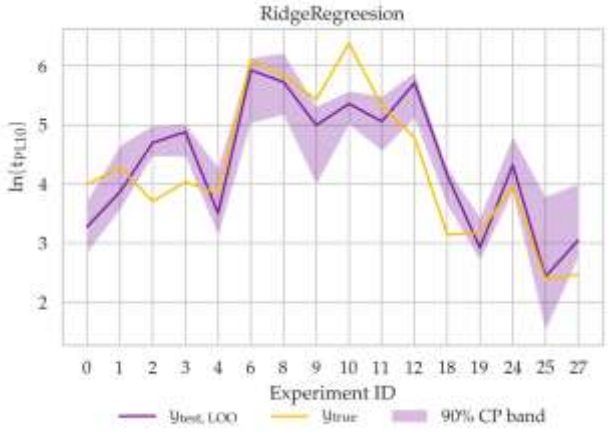
[2] Barber, Rina Foygel, et al. "Predictive inference with the jackknife+." arXiv preprint arXiv:1905.02928 (2019).

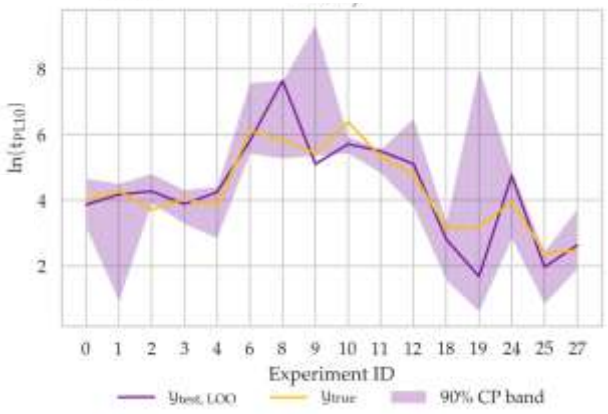
Conformal Prediction (CP) bands for $MAPbI_3$ degradation

- Predict: t_{PL10} (time when PL drops to 10% of initial value)
- Out of sample prediction (testing): *leave-one-out*
- Uncertainty quantification: 90% conformal prediction (CP) band

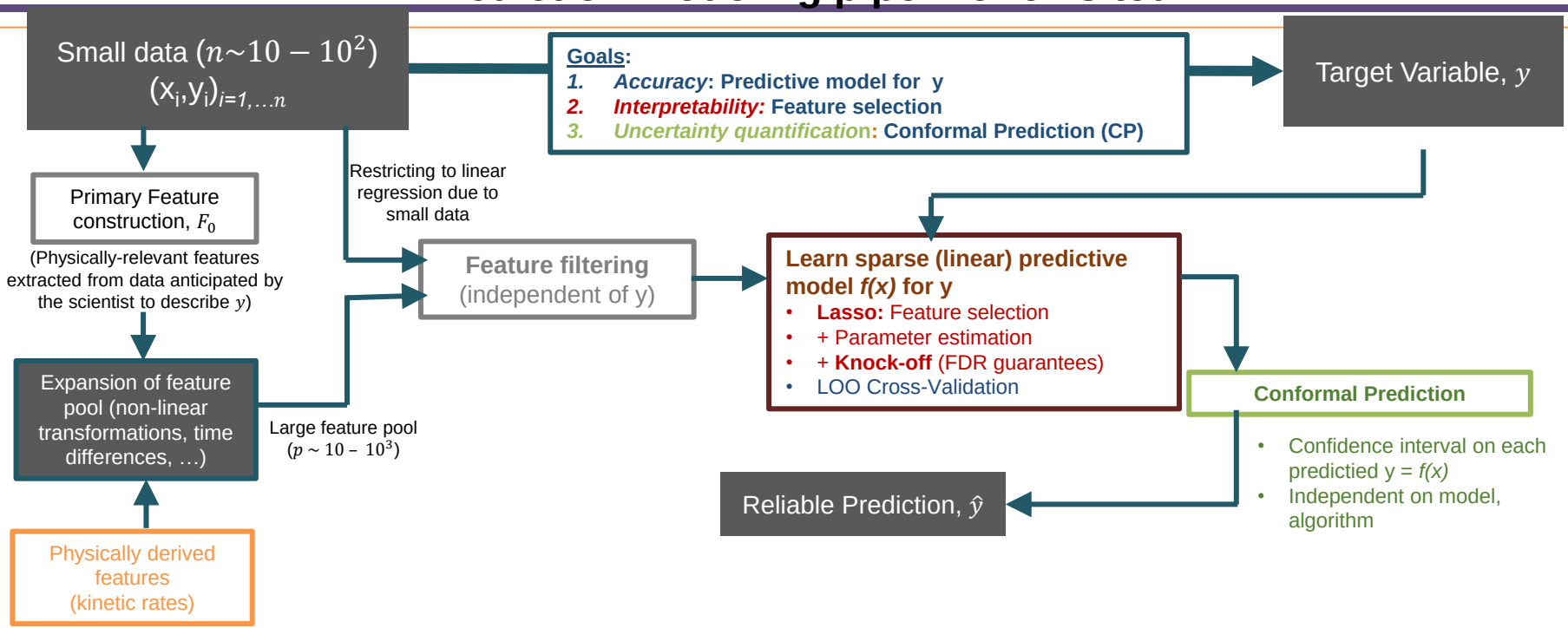








Prediction modeling pipeline revisited



- Informational limits on degrees of freedom $s \log p$
- Learning physically meaningful features from independent experiments (hierarchical modeling)
- Sparse Linear Regression (Lasso)
- Controlling the FDR with the Knock-offs filter
- Uncertainty quantification by Conformal Prediction

Role of ML/AI expert

ML/AI expert

- What is statistically possible (and what is not)
- What methods are applicable (and which are not)
- Access and rapid percolation of **state of the art results** (methods, theories, …)
  - AI, ML, Statistics are fast developing
- View of the **entire data analysis pipeline**
  - New ML results are specialized
- Optimize **statistical power** (get as much as possible from the given data/experiment)
- Validation
  - Are predictions accurate? What part of model can be trusted/generalized to other problems?

In-house

- Algorithms and methods
- Feature construction and transformation
- Exploratory data analysis
- Range of measurements, SNR, sample sizes (=experimental constraints)
- Performance requirements
  - Level of accuracy

Conclusions

Statistical and ML strategies for valid inferences from small data

- Informational limits on degrees of freedom $s \log p$ [2004]
- Learning physically meaningful features from independent experiments (hierarchical modeling)
  - Increase complexity, allows non-linearity
- Sparse Linear Regression [~2004]
- Controlling the FDR with the Knock-offs filter [2018]
- Uncertainty quantification by Conformal Prediction [2014]

Thank you!

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Motivation

1. Need for Machine Learning in Applied Sciences

- Often, in applied research, mathematical relations describing the physiochemical properties and mechanisms are important for a deeper understanding.

- However, theoretical first-principle based calculations are often *computationally expensive* and are biased with several a priori assumptions.

- Hence recently, ***machine learning methods*** that can learn trends from ***experimental data*** have grown popular due to their ease,

Most models are built to predict material properties obtained from experiments using non-experimental features. Hence, the ***size of these datasets are restricted by the complexity and the time scales of these experiments.***

Table 1. Summary of material properties predicted with machine learning methods and corresponding references

Property	References
Curie temperature	31,283–287
Vibrational free energy and entropy	288
Band gap	40,41,132,159,283,289–300
Dielectric breakdown strength	38,44,45
Lattice parameter	300
Debye temperature and heat capacity	41–43
Glass transition temperature	301,302
Thermal expansion coefficient	41
Thermal boundary resistance	303
Thermal conductivity	37,46–51,304,305
Local magnetic moments	127,306
Melting temperature	39,48,307
Magnetocaloric effects	283
Grain boundaries	308
Grain boundary energy	309–312
Grain boundary mobility	312
Interface energy	300
Seebeck coefficient	46,313,314
Thermoelectric figure of merit	315
Bulk and shear moduli	40–42,132,184,185,316
Electrical resistivity	46
Density of states	109,317,318
Fermi energy and Poisson ratio	40
Dopant solution energy	319
Metal–insulator classification	61
Topological invariants	320–326
Superconducting critical temperature	73,76,122,327–329
Li-ion conductivity and battery state-of-charge	65,330,331

Schmidt, J., Marques, M.R.G., Botti, S. et al. *Recent advances and applications of machine learning in solid-state materials science*. npj Comput Mater 5, 83 (2019).

Motivation

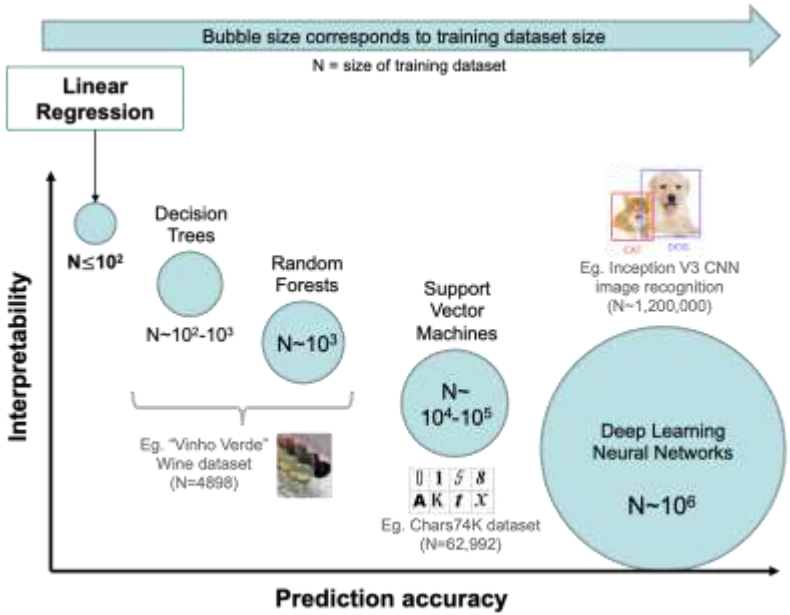
2. Small datasets from experiments

- Most data sets in engineering and medicine are small (N_{data}~ 10^1 - 10^2) compared to the general ML standards (N_{data} > 10^3).

- This calls for attention towards often machine learning techniques such as ***generalized linear regression*** etc. that can handle such small datasets.

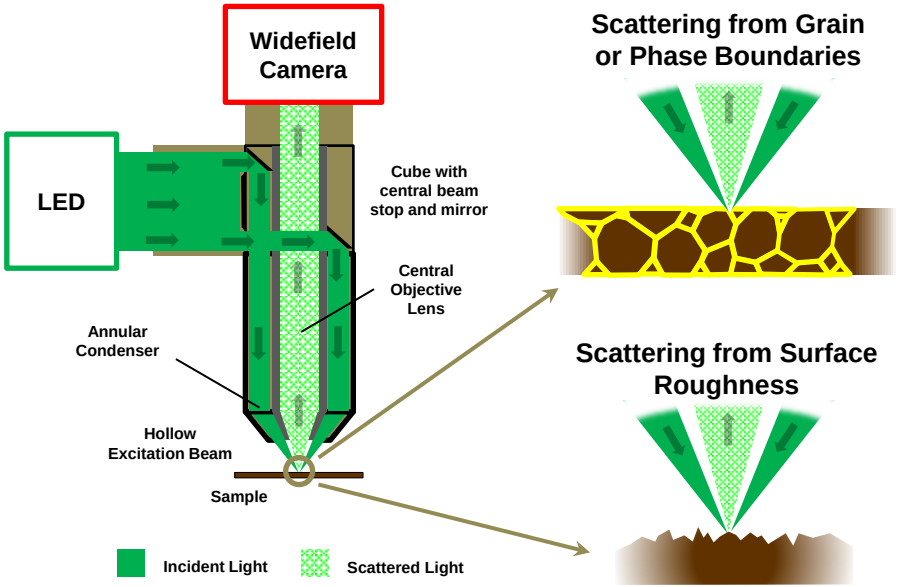
- Along with **the choice of the learning method**,
  - **the choice of features and the relevant target variable to describe the desired phenomenon,**
  - **the model testing protocol,**
  - **the metrics to interpret the final models to understand the underlying phenomenon**

  are important for every such dataset.

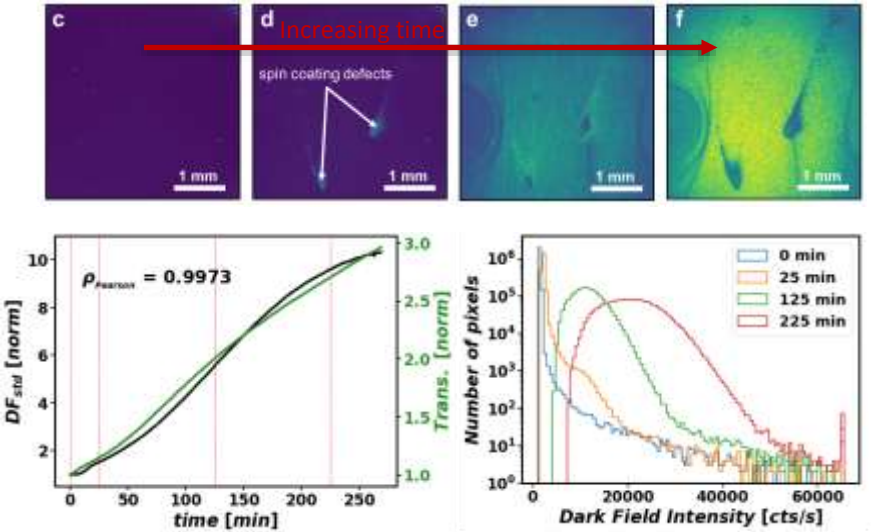


Hence, there is a need in the scientific community for machine learning techniques that can be used on small datasets.

Features in Dark-Field Microscopy Images Reveal Rate of Degradation



Degradation of $MAPbI_3$ film at 25 °C, 60 %RH, 21 $\%O_2$, 8 Sun illumination



Dark-field image intensity and heterogeneity are both highly correlated with transmittance and can be used as ***features for forecasting perovskite PV device performance.***

We pondered… What can we learn (quantitatively) about the rate of degradation from transmittance and reflectance?

R.J. Stoddard, W. Dunlap-Shohl, H. Qiao, Y. Meng, W. Kau, and H.W. Hillhouse, *ACS Energy Lett.* **2020,** 5, 3, 946

Timeline of DOE Milestones and GNGs

		Year 1			Year 2				Year 3			
		Sept 2021	Dec 2021	Mar 2022	June 2022	Sept 2022	Dec 2022	Mar2022	June 2023	Sept 2023	Dec	Mar 2024
Task 1. Forecasting the Absorber-Quality-Limited Lifetime for High-Bandgap and Low Bandgap Materials (L_d-T80)												
	1.1. Data Collection	M1.1	M1.2									
	1.2. Feature Selection			M1.3								
	1.3. Forecasting Model					GNG1						
Task 2. Forecasting Low-Bandgap Sub-Cell PCE												
	2.1. Data Collection			M2.1								
	2.2. Feature Selection				M2.2							
	2.3. Forecasting Model					GNG2						
Task 3. Forecasting High-Bandgap Sub-Cell PCE												
	3.1. Data Collection						M3.1					
	3.2. Feature Selection							M3.2				
	3.3. Forecasting Model								M3.3			
Task 4. Forecasting Tandem T80												
	4.1. Data Collection							M4.1				
	4.2. Feature Selection								M4.2			
	4.3. Forecasting Model									M4.3		
	4.4. Field Deployment											M4.4
Task 5. Dissemination and Data Accessibility												
						GNG3						M5.1

Hougen-Watson-Langmuir-Hinshelwood (HWLH) Equations

Any single-step heterogenous reaction as shown below, can be written using the following three steps:

Overall Reaction: $\boldsymbol{aA + bB \rightarrow rR + sS}$

$$aA \rightarrow aA^*$$
$$bB \rightarrow bB^*$$

Step-1: Langmuir adsorption of the gaseous reactants A & B

$$aA^* + bB^* \rightarrow rR^* + sS^*$$

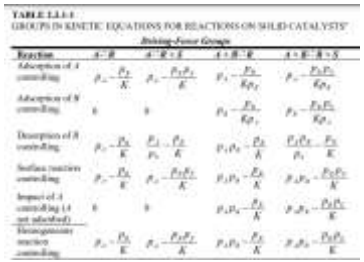
Step-2: Surface reaction of the adsorbed A & B to adsorbed R & S

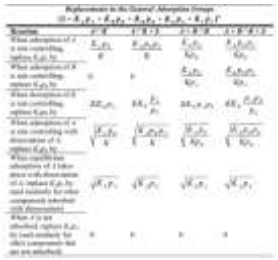
$$rR^* \rightarrow rR$$
$$sS^* \rightarrow sS$$

Step-3: Langmuir desorption of the gaseous products R & S

Hougen and Yang [1] used the principles of the HWLH Equations to build a generalized rate expression. Every rate equation for a mechanism like above can be written in the form **if a RDS is assumed**:

$$rate = \frac{(\text{kinetic} - \text{group}) \times (\text{driving force} - \text{group})}{(\text{adsorption group})}$$





This means for a given set of A, B, R and S-

- **if the parameters (a, b, r, s) of the system of rate equations are known and,**
- **the RDS is assumed,**

the overall rate expression can be easily written.

Yang, K. H., and Hougen, 0. A., "Determination of Mechanism of Catalyzed Gaseous Reactions," Chem. Eng. Prog., 46,146 (1950).

Potential for Langmuir-Hinshelwood-Hougen-Watson (LHHW) equations for use in perovskite-gas heterogenous reactions

The original[1] sets of LHHW have until been applied only for simple ***single-step solid-catalyzed heterogeneous reactions***. With subtle adjustments, these equations can further be generalized to be applied for reactions occurring at the perovskite-gas interfaces.

Domain of applicability of LHHW equations:

1. **Gases reacting on a solid surface** → For perovskites, water and O_2 react on the surface.
2. **The active sites on the solid surface are invariant** → For early-times we use, the active site concentration on the perovskite can be assumed to be constant. Although perovskite is involved in the reaction, very minimal change in the activity of the perovskite can be assumed.
3. **Monolayer Langmuir adsorption and desorption** of gaseous reactants and products → Reasonable assumption for perovskites under the operating environmental conditions.
4. The charge-transfer reactions can be assumed to be **fast and always in quasi-equilibrium**.

A: O_2

1A: Generation of adsorbed A species†

$$K_{A0}: \quad A_{mol} + \alpha[*] \rightleftharpoons \alpha\, A^*$$

$$K_{A1}: \quad A^* + e^- \rightleftharpoons A^{*-}$$
$$K_{A2}: \quad A^{*-} + e^- \rightleftharpoons A^{*2-}$$
$$K_{A3}: \quad A^{*2-} + e^- \rightleftharpoons A^{*3-}$$
$$\vdots$$
$$K_{Ax}: \quad A^{*(x-1)-} + e^- \rightleftharpoons A^{*x-}$$

B: H_2O

1B: Generation of adsorbed B species

$$K_{B0}: \quad B_{mol} + \beta[*] \rightleftharpoons \beta\, B^*$$

$$K_{B1}: \quad B^* + e^- \rightleftharpoons B^{*-}$$
$$K_{B2}: \quad B^{*-} + e^- \rightleftharpoons B^{*2-}$$
$$K_{B3}: \quad B^{*2-} + e^- \rightleftharpoons B^{*3-}$$
$$\vdots$$
$$K_{By}: \quad B^{*(y-1)-} + e^- \rightleftharpoons B^{*y-}$$

2: Surface reaction†

$$K_{SR}: \quad \text{perov. (solid)} + a\, A^{*p-} + b\, B^{*q-} + k\, e^- + s\,[*] \rightleftharpoons \text{other/perov. (solid)} + c_1 C_1^* + \cdots + c_{sr} C_{sr}^*$$

3: Desorption of products‡

$$K_{C_i}: \quad C_{i,mol} + \kappa_i[*] \rightleftharpoons \kappa_i\, C_i^*$$

† The charge transfer reactions are assumed to be fast, and always in quasi-equilibrium.
‡ Desorbed products are shown on the left to indicate that the equilibrium constant is defined with the adsorption as the forward reaction.

1. Hougen, O. A., And Watson, K. M., "Chemical Process Principles," Vol. 3. Wiley, New York, 1947.

Generalized LHHW equations for use in perovskite-gas heterogenous reactions

Rate controlling step	Rate expression
1A. A0 controlling: (Adsorption of A)	$r = \dfrac{k'_{A0}\, p_A}{\left[1 + p_B^{1/\beta}\left(K'_{B0} + K'_{B1} n + K'_{B2} n^2 + \cdots + K'_{By} n^y\right)\right]^{\alpha}}$
1B. B0 controlling: (Adsorption of B)	$r = \dfrac{k'_{B0}\, p_B}{\left[1 + p_A^{1/\alpha}\left(K'_{A0} + K'_{A1} n + K'_{A2} n^2 + \cdots + K'_{Ax} n^x\right)\right]^{\beta}}$
2. SR controlling:	$r = \dfrac{k'_{S2} \cdot p_A^{a/\alpha} \cdot p_B^{b/\beta} \cdot n^{(pa+qb+k)}}{\left[\begin{array}{l}1 + p_A^{1/\alpha}\left(K'_{A0} + K'_{A1} n + K'_{A2} n^2 + \cdots + K'_{Ax} n^x\right) \\ + p_B^{1/\beta}\left(K'_{B0} + K'_{B1} n + K'_{B2} n^2 + \cdots + K'_{By} n^y\right)\end{array}\right]^{a+b+s}}$
3A: C_i controlling and is the only gaseous product: (Desorption of C_i)	$r = \dfrac{k'_{-C_i} \cdot \left(p_A^{a/\alpha} \cdot p_B^{b/\beta} \cdot n^{(pa+qb+k)}\right)^{\kappa_i/c_i}}{\left[\begin{array}{l}1 + p_A^{1/\alpha}\left(K'_{A0} + K'_{A1} n + \cdots + K'_{Ax} n^x\right) + \\ p_B^{1/\beta}\left(K'_{B0} + K'_{B1} n + \cdots + K'_{By} n^y\right) \\ + K'_{SR} \cdot \left(p_A^{a/\alpha} \cdot p_B^{b/\beta} \cdot n^{(pa+qb+k)}\right)^{1/c_i}\end{array}\right]^{\kappa_i}}$
3B: C_i controlling (Desorption of C_i)	$r = k''_{-C_i}$

A given parameter set = ϕ

$\{\alpha, \beta, a, b, x, y, p, q, k, s, c_i \kappa_i\}$

+

Rate-determining step (RDS)

↓

Rate expression

$r_{RDS}(p_A, p_B, n, \phi)$

After placing restraints on the parameter combinations, a total of <u>132</u> candidate sets are obtained.