Towards completing chemistry sets for plasma simulations

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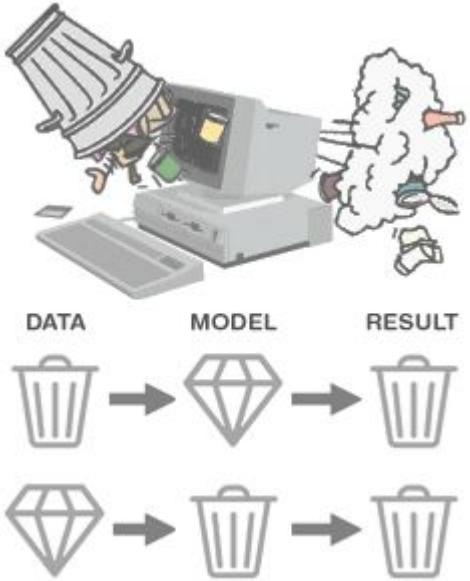
Introduction

Simulations are widely used in both academic and industrial settings to gain insight into and optimize plasma processes.



The success of such investigations hinges on having good data for the chemical processes in form of:

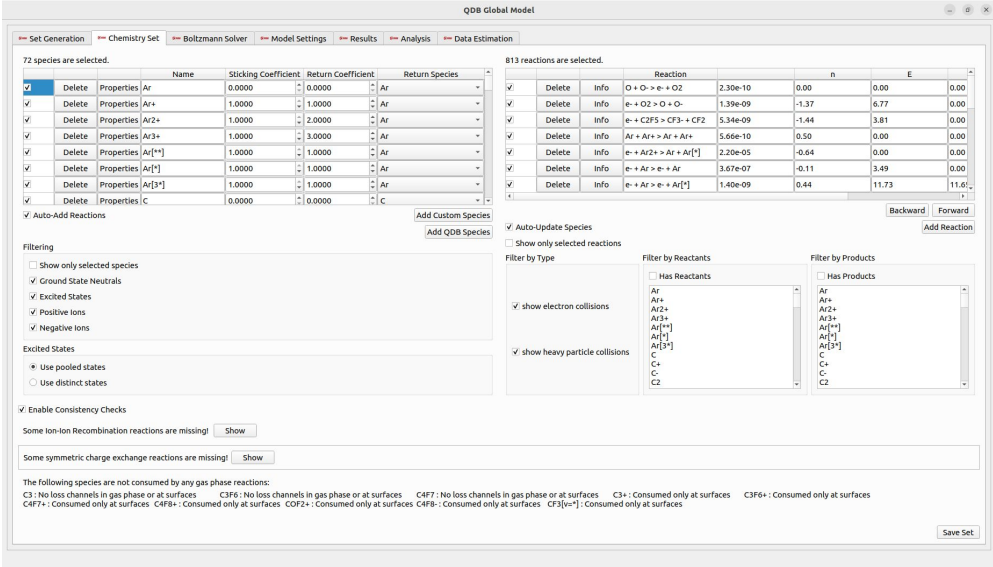
- Cross sections
- Rate coefficients
- Coefficients for surface processes

Data can be found in individual publications or databases such LXCat, UMIST,KIDA,NFRI,NIFS, or Quantemol-DB.

Constructing a set via QDB

To construct a complete set, we offer our chemistry generator which automatically finds all relevant gas phase reactions for a specified gas mixture. The resulting sets might have some missing data, among them:

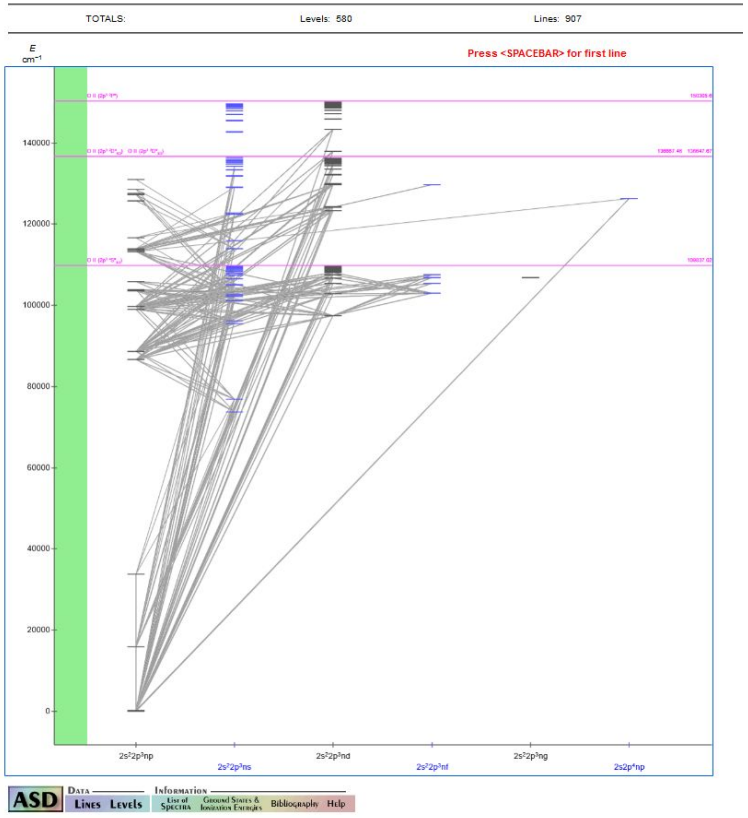
- Radiative processes
- Unknown heavy particle reactions
- Unknown electron collisions



Filling the gap

Radiative Processes

Radiative Databases



The NIST atomic spectra database gives access to radiative transition for atoms. States are finely resolved 120 000 transitions are stored in this database.

https://www.nist.gov/pml/atomic-spectra-database

The ExoMol database gives access to radiative transitions for molecules. States again are again finely resolved leading to over 1 trillion transitions for currently 85 molecules.

LiDb - Lifetime Database

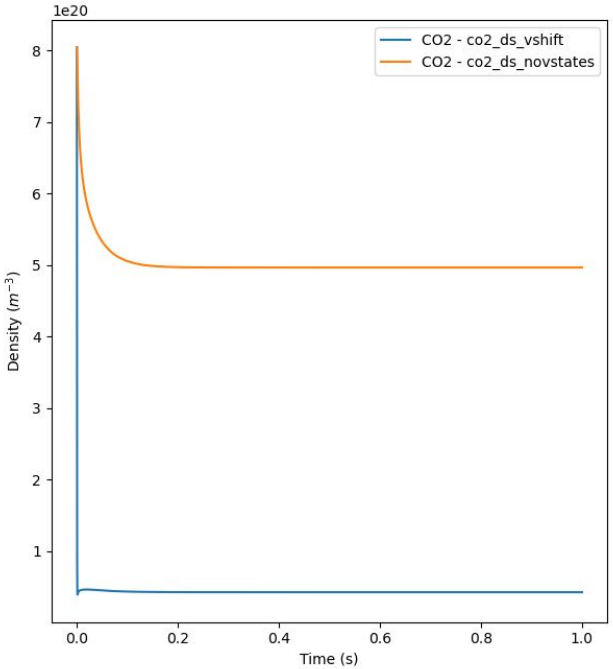
LiDb offers data from NIST and ExoMol processed for more convenient use in plasma modelling by:

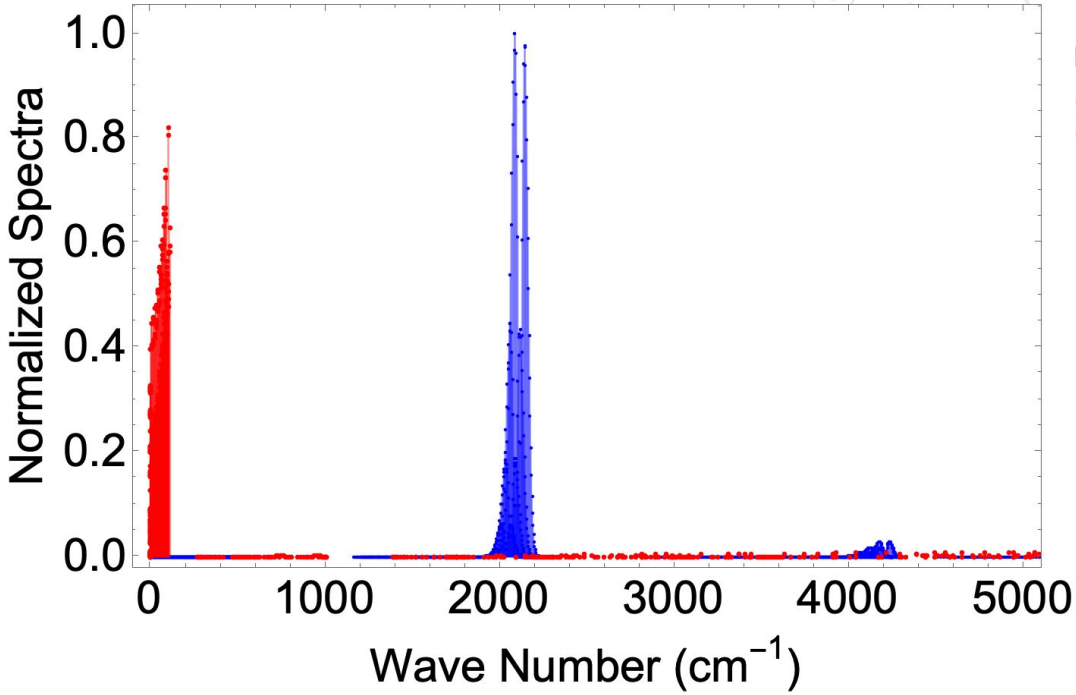
a) Lumping the finely resolved states, e.g. neglecting rotational resolution for vibrational states.
b) Providing total lifetimes as well partial lifetimes/branching ratios to specific target states.
c) Provide an API for easy access and integration into QDB.

v=1	v=2	v=3	v=4
J=1	J=1	J=1	J=1
J=2	J=2	J=2	J=2
J=3	J=3	J=3	J=3
J=4	J=4	J=4	J=4
…	…	…	…

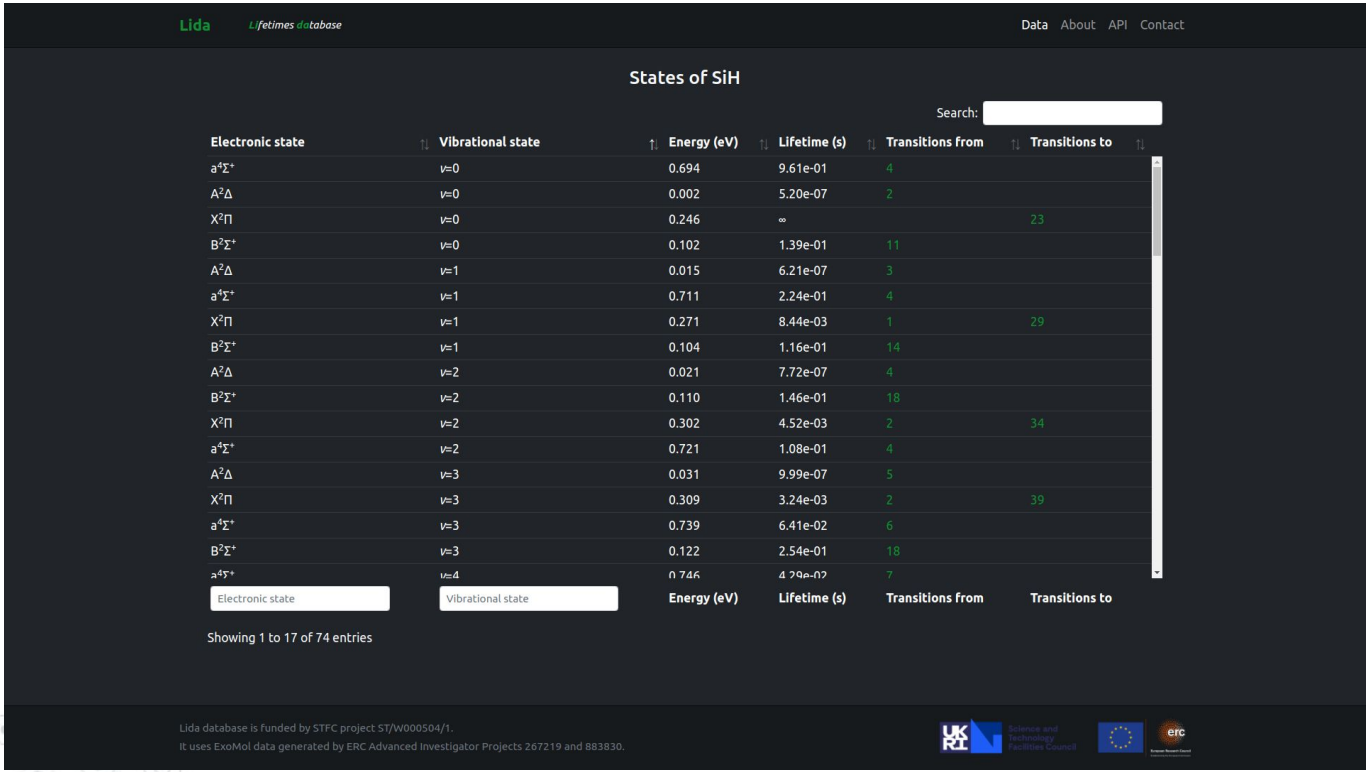
v=1	v=2	v=3	v=4

Use case: CO_2 global plasma simulations





LiDb example page



https://www.exomol.com/lidb

Filling the gap

Heavy Particle Reactions

Heavy particle collisions

Plasma chemistry is heavily governed by heavy particle reactions such as:

- Charge Exchange
- Ion-Ion Recombination
- Neutral-Neutral Reactions

When data are missing one can:

- Estimate data in analogy to similar reactions
- Calibrate the missing rate coefficients to match experimental results
- Calculate them numerically

However, these methods are either rather inaccurate or time-consuming

ML estimator for rate coefficients

quantemol

Heavy particle collisions

$$A + B \longrightarrow C + D$$

Machine learning model

Target:

Rate coefficients, **k** ~ 10^{-40} - 10^{-5} at 300 ± 30 K

~12500 reactions collected from **KIDA, NFRi, Umist** and **QDB** databases

Input features:

- mass, **m**
- charge, **q**
- standard enthalpy of formation, $\Delta_f H^0$
- polarizability, **α**
- dipole moment, **p**
- enthalpy of formation of a neutral counterparts to charged species, $\Delta_f H^0_{neut}$
- ionisation energy of neutral species
- species elemental composition data

Results: ML estimator for rate coefficients

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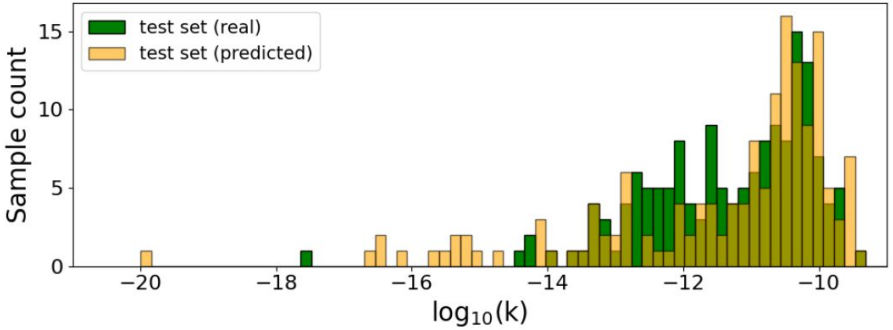
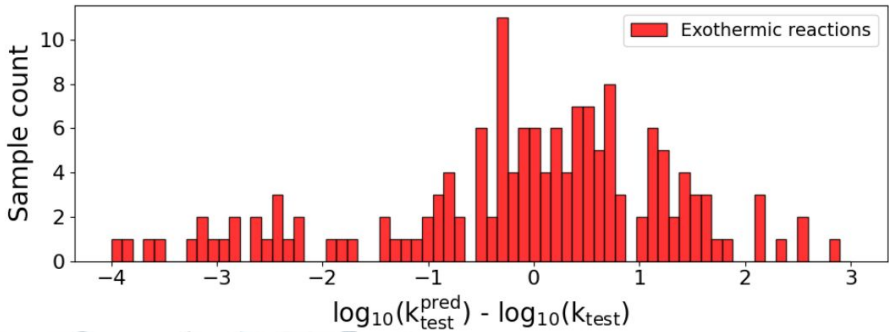
Reactions like $A + B \longrightarrow C + D$

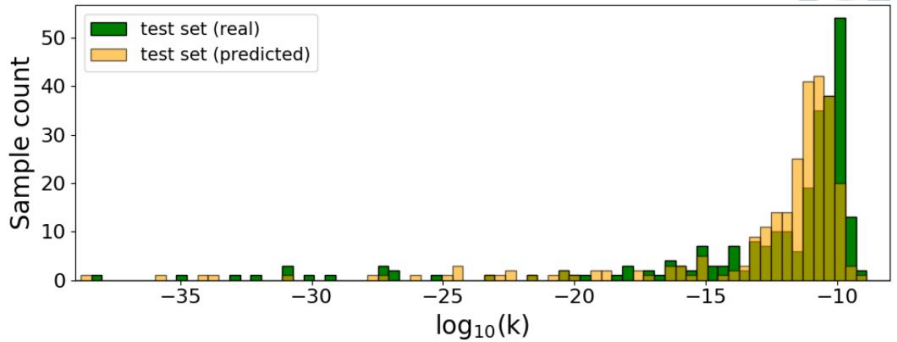
ΔH < 0: 173 test reactions



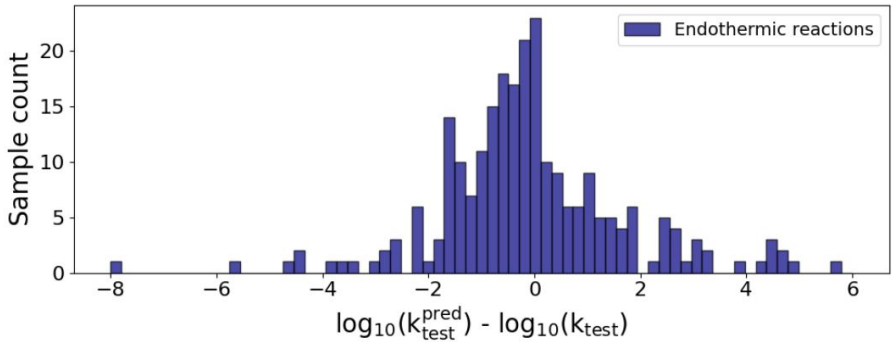
Mean Absolute Error on test data: **1.15**



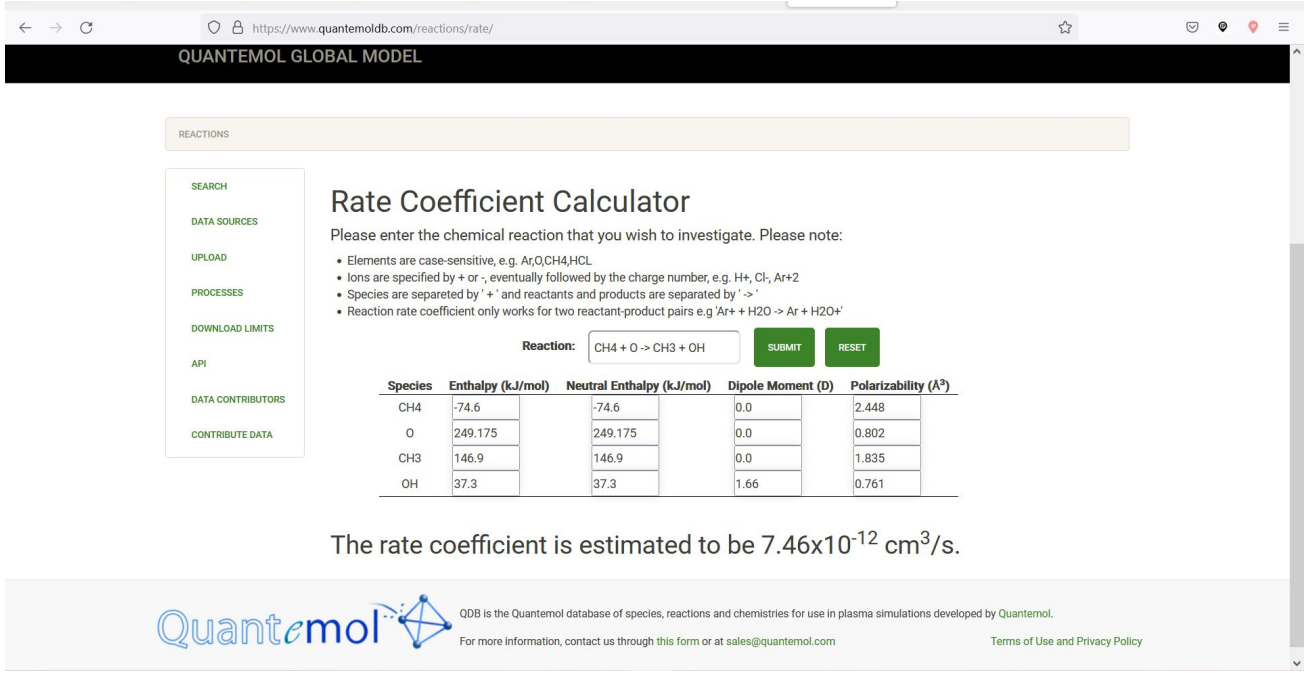
ΔH > 0: 274 test reactions



Mean Absolute Error on test data: **1.17**



Using the rate coefficient estimator



https://www.quantemoldb.com/reactions/rate-coefficient-estimator/

Filling the gap

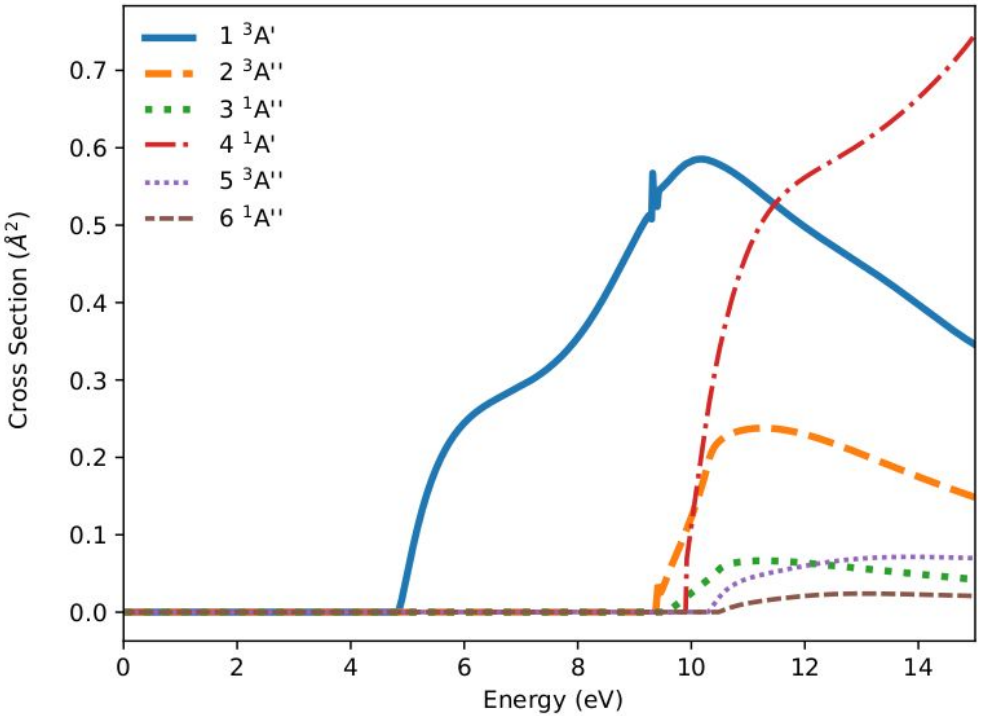
Branching Ratios

Electron collisions

Cross- sections for electron-molecule cross-sections can be calculated precisely via different methods (BEB,R-Matrix etc.)

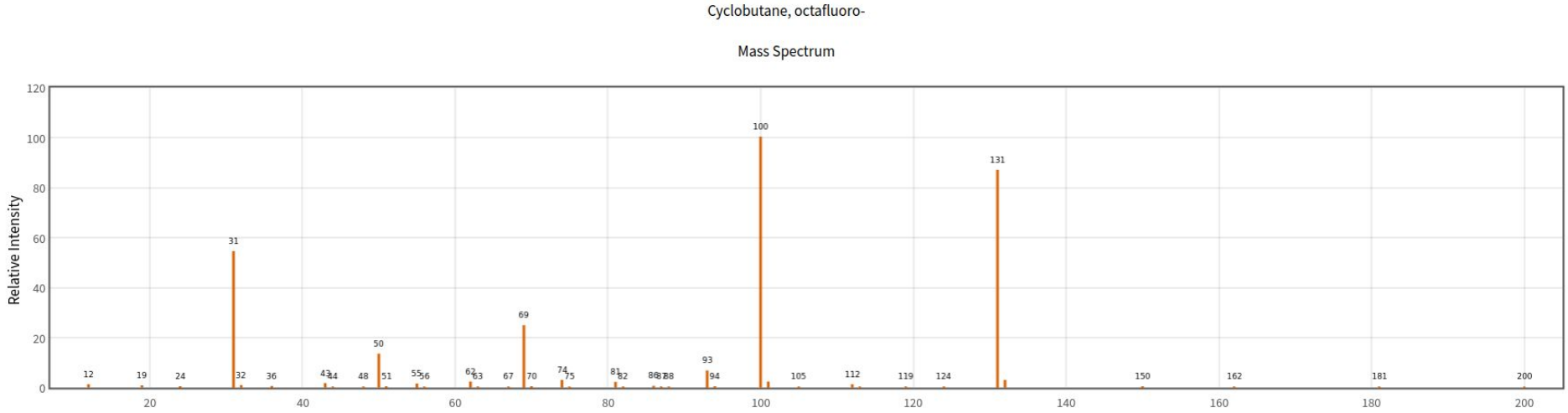
For ionization and dissociation, these calculations do not yield the fragmentation patterns!

Electronic Excitation for $C_3H_2F_4$



How to determine fragments - Dissociative Ionization

- Mass spectra in combination with bond strengths/appearance potentials can be used to split up the total ionization



https://webbook.nist.gov/cgi/cbook.cgi?ID=C115253&Units=SI&Mask=200#Mass-Spec

Prediction of electron impact ionisation fragmentation patterns

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Input features

SMILES

Numeric features

Molecular features:

- molecular mass
- total N atoms
- total N bonds

Bond features:

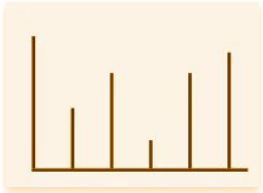
- bond types (single,double,..)
- bond chirality (e,z,unknown,none)
- bonds in rings
- conjugated bonds

Atomic features:

- atom types (C, O, N, S …)
- atom valence
- number of neighbours
- atom hybridization
- atom aromaticity

Machine learning model training

Target



Mass spectrum vectors
y=(y1, y2 , … yn)

Prediction of electron impact ionisation fragmentation patterns

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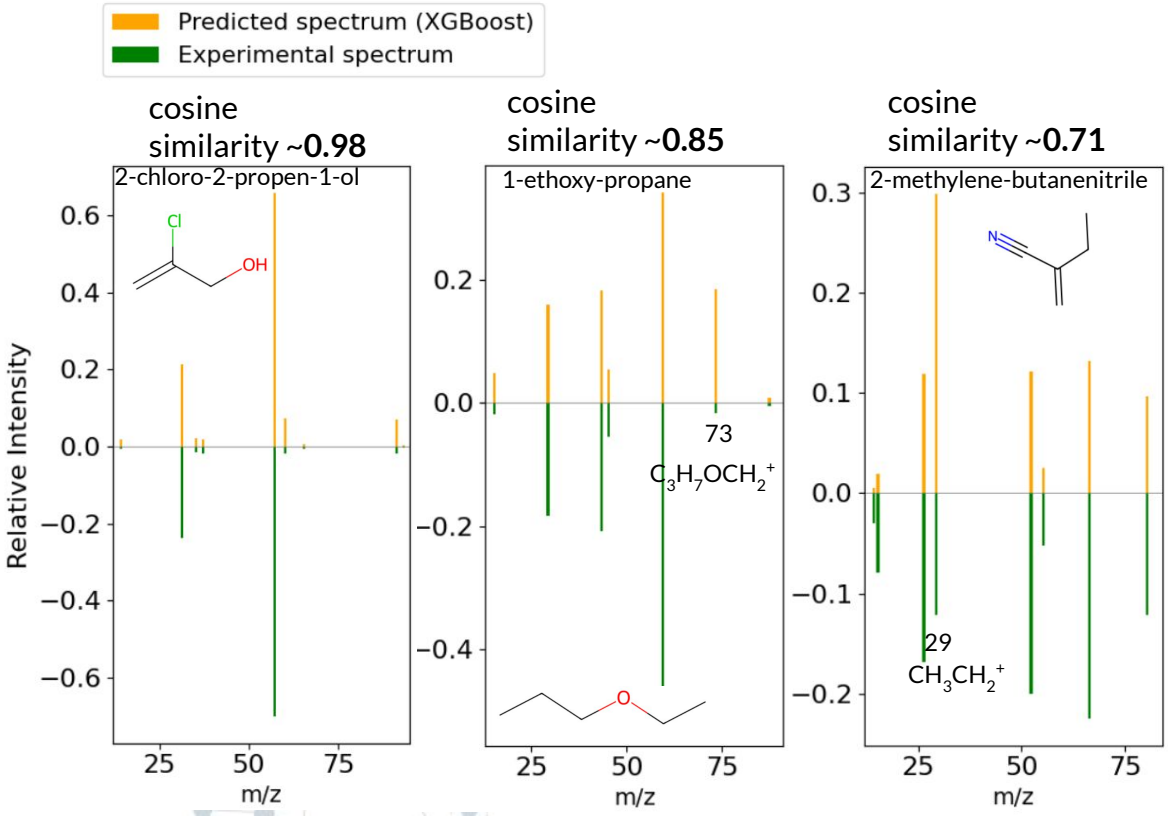
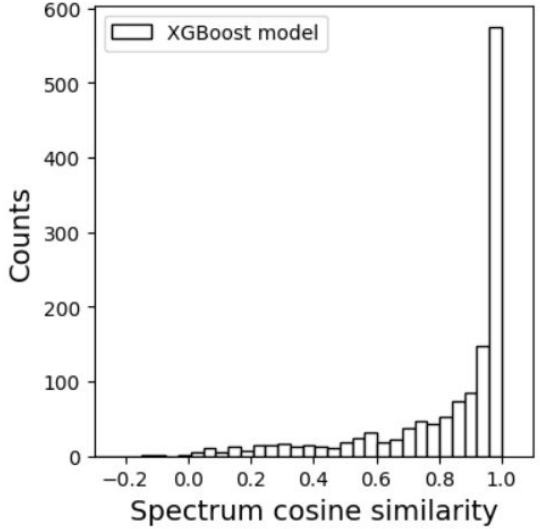
Evaluation metric: cosine similarity between real and predicted mass spectra



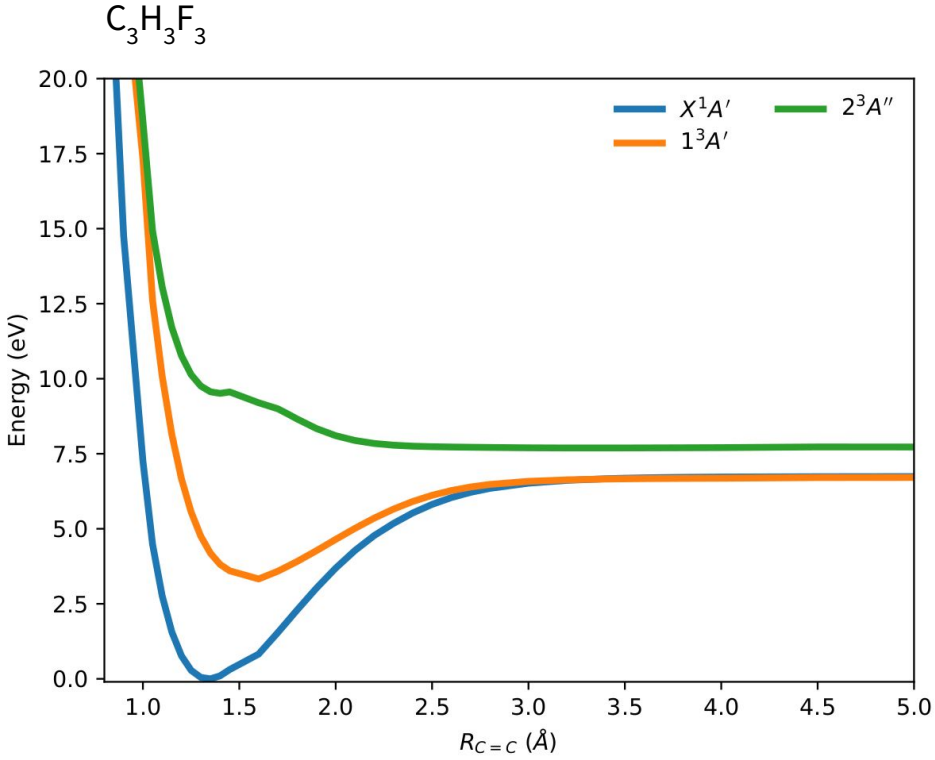
The best performing model so far



For ~80% of compounds in the test set cosine similarity is greater than 0.7

How to determine fragments - Neutral Dissociation

- Analysing potential curves can tell you which dissociation pathways from a given state are possible, but not whether they actually happen or in which ratio.



Explanation

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- Time dependent Schroedinger equation is solved for motion of the nuclei in the molecule.
- The resulting trajectories of nuclei determine which bonds are broken after the excitation to an excited state.
- The computations are repeated with random initial conditions.
- We count how often a specific bond gets broken.

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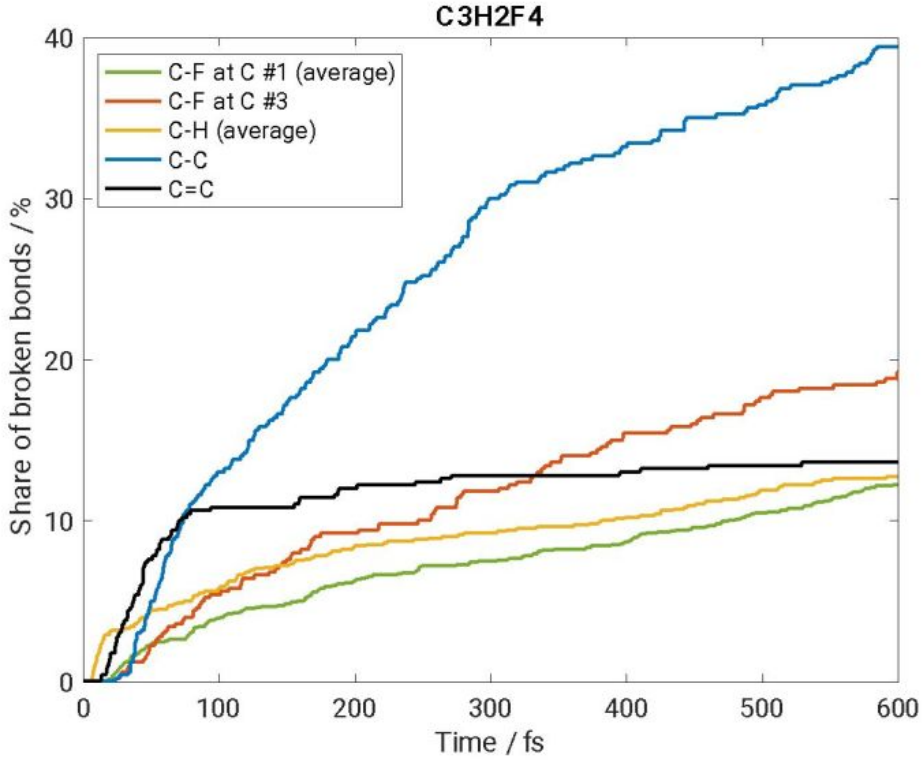
Results for $C_3H_2F_4$



Product	P
F	0.49
CF_3	0.36
C_2H_2F	0.25
H	0.22
$C_3H_2F_3$	0.20
CHF	0.13

Summary and Outlook

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To close data gaps in our database we are working on:

- LiDb, a database for radiative processes prepared in a format suitable for plasma simulations
  - Add atomic transitions
- A Machine Learning algorithm for a quick estimation of heavy particle rate coefficients
  - Likely needs more data to improve performance
- A Machine Learning algorithm to estimate ionization mass spectra of molecules
  - Good initial results, currently implementing it into our services
- Ab Initio Method to calculate branching ratios for electron impact neutral dissociation
  - First results soon to be published

Thank you for your attention.