



# Towards completing chemistry sets for plasma simulations

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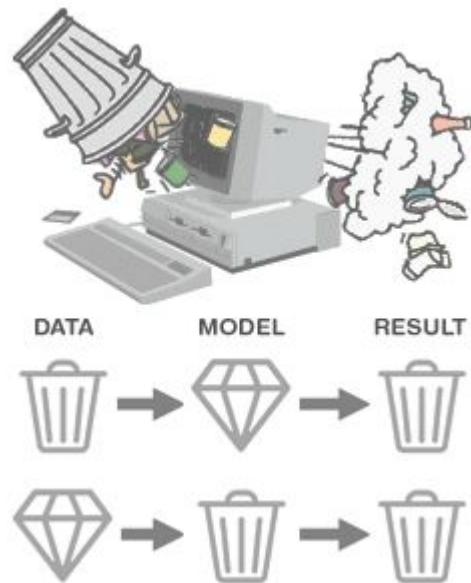
# Introduction

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

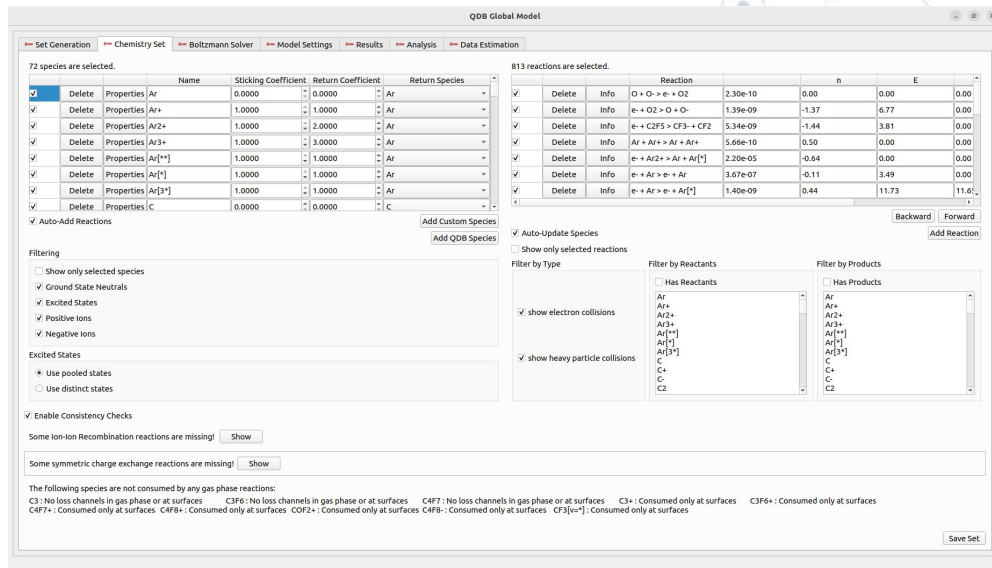
Data can be found in individual publications or databases such LXCat, UMIST, KIDA, NFRI, NIFS, or Quantemol-DB.



# 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



The screenshot displays the 'QDB Global Model' software interface. The 'Set Generation' tab is active, showing a table of 72 species and 813 reactions. The table includes columns for Name, Sticking Coefficient, Return Coefficient, and Return Species. Below the table, there are sections for 'Filtering' (Show only selected species, Ground State Neutrals, Excited States, Positive Ions, Negative Ions), 'Excited States' (Use pooled states, Use distinct states), and 'Enable Consistency Checks'. The 'Auto-Add Reactions' and 'Auto-Update Species' checkboxes are checked. The 'Filter by Type' section shows 'show electron collisions' and 'show heavy particle collisions' selected. The 'Filter by Reactants' and 'Filter by Products' sections show lists of species. At the bottom, there are links to 'Show' missing ion-ion recombination and symmetric charge exchange reactions, and a 'Save Set' button.

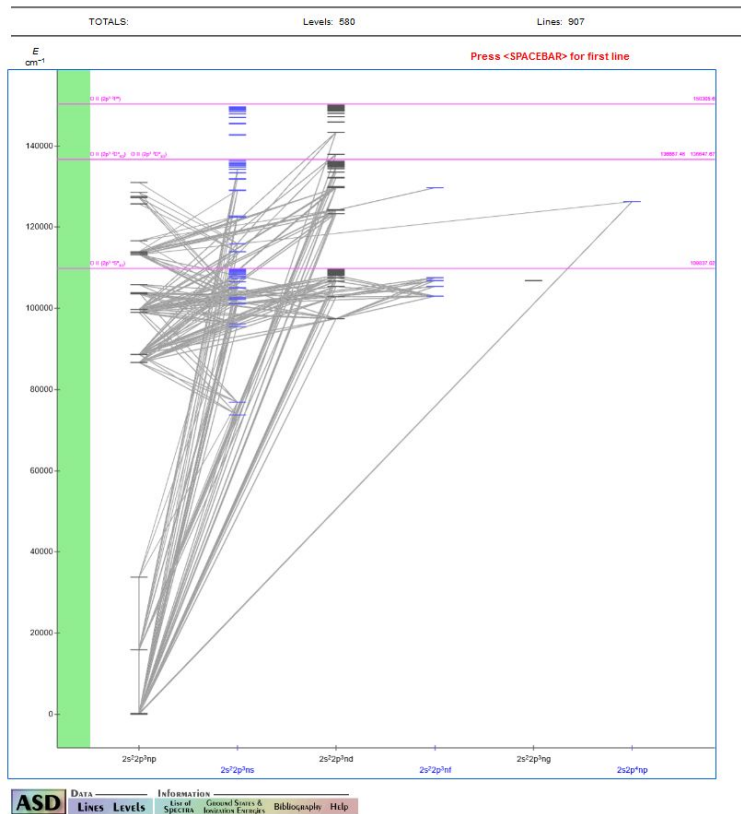


Filling the gap

# 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:

- Lumping the finely resolved states, e.g. neglecting rotational resolution for vibrational states.
- Providing total lifetimes as well partial lifetimes/branching ratios to specific target states.
- 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
...	...	...	...

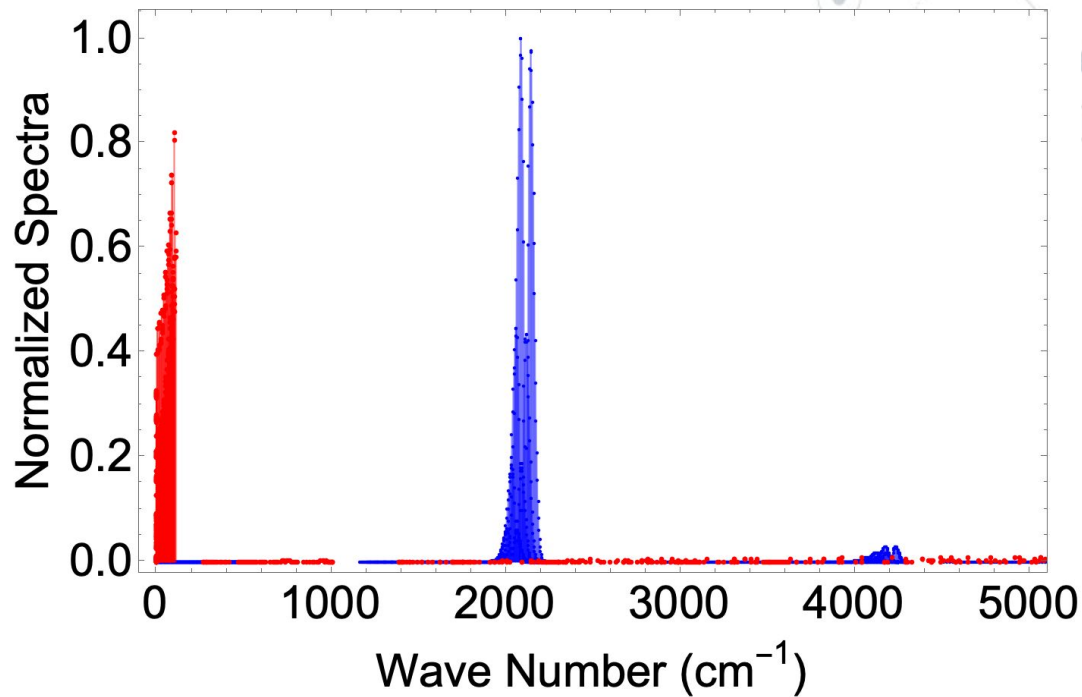
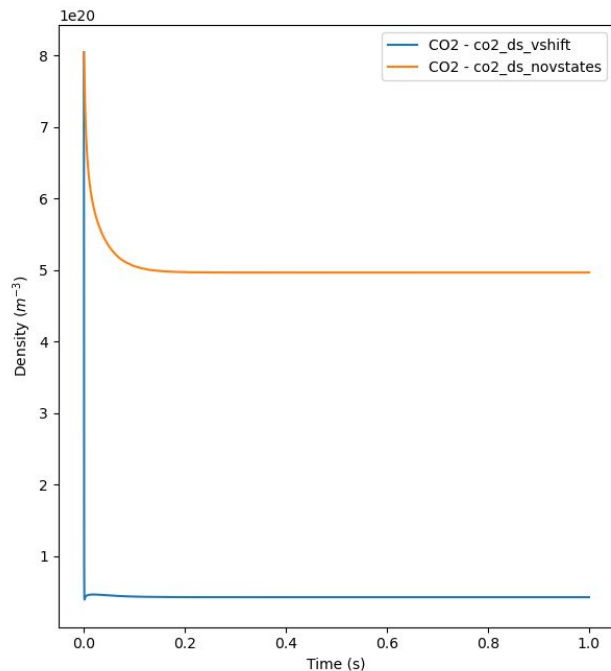


v=1	v=2	v=3	v=4
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# Use case: CO<sub>2</sub> global plasma simulations



quantemol



# LiDb example page

LiDb Lifetimes database

Data About API Contact

### States of SiH

Search:




Electronic state	Vibrational state	Energy (eV)	Lifetime (s)	Transitions from	Transitions to
$a^4\Sigma^+$	$v=0$	0.694	$9.61e-01$	4	
$A^2\Delta$	$v=0$	0.002	$5.20e-07$	2	
$X^2\Pi$	$v=0$	0.246	$\infty$		23
$B^2\Sigma^+$	$v=0$	0.102	$1.39e-01$	11	
$A^2\Delta$	$v=1$	0.015	$6.21e-07$	3	
$a^4\Sigma^+$	$v=1$	0.711	$2.24e-01$	4	
$X^2\Pi$	$v=1$	0.271	$8.44e-03$	1	29
$B^2\Sigma^+$	$v=1$	0.104	$1.16e-01$	14	
$A^2\Delta$	$v=2$	0.021	$7.72e-07$	4	
$B^2\Sigma^+$	$v=2$	0.110	$1.46e-01$	18	
$X^2\Pi$	$v=2$	0.302	$4.52e-03$	2	34
$a^4\Sigma^+$	$v=2$	0.721	$1.08e-01$	4	
$A^2\Delta$	$v=3$	0.031	$9.99e-07$	5	
$X^2\Pi$	$v=3$	0.309	$3.24e-03$	2	39
$a^4\Sigma^+$	$v=3$	0.739	$6.41e-02$	6	
$B^2\Sigma^+$	$v=3$	0.122	$2.54e-01$	18	
$a^4\Sigma^+$	$v=4$	$n 746$	$4 79e-02$	7	

Electronic state  Vibrational state

Energy (eV) Lifetime (s) Transitions from Transitions to

Showing 1 to 17 of 74 entries

LiDb database is funded by STFC project ST/W000504/1.  
It uses ExoMol data generated by ERC Advanced Investigator Projects 267219 and 883830.

 Science and Technology Facilities Council  

<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

Heavy particle collisions



## Machine learning model

### Target:

Rate coefficients,  $k \sim 10^{-40} - 10^{-5}$   
at  $300 \pm 30$  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,  $\alpha$
- 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

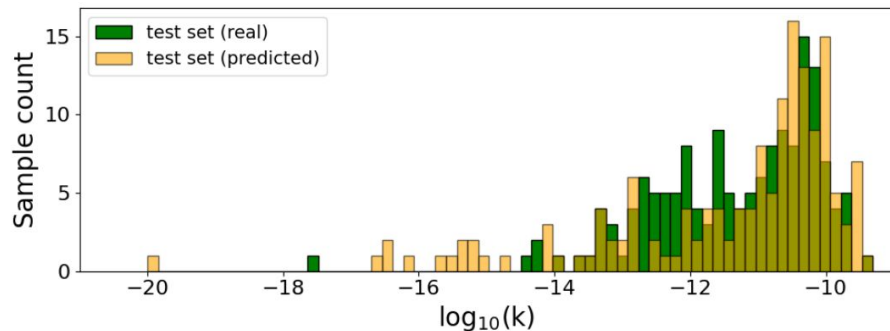
# Results: ML estimator for rate coefficients



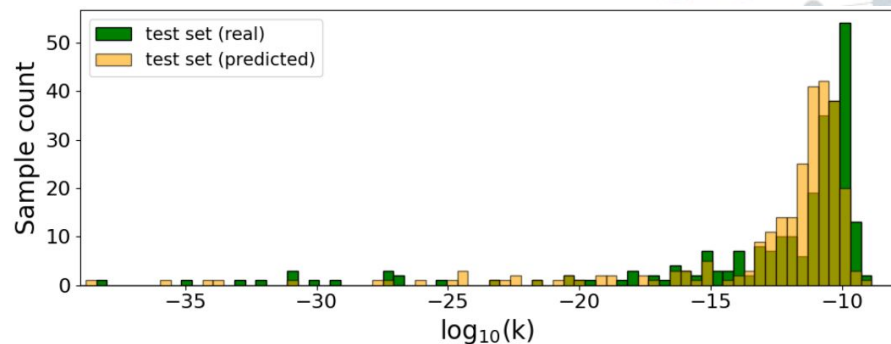
Reactions like  $A + B \rightarrow C + D$

$\Delta H < 0$ : 173 test reactions

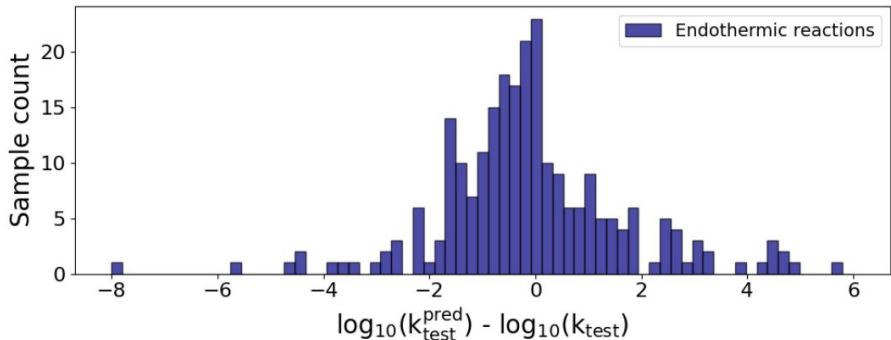
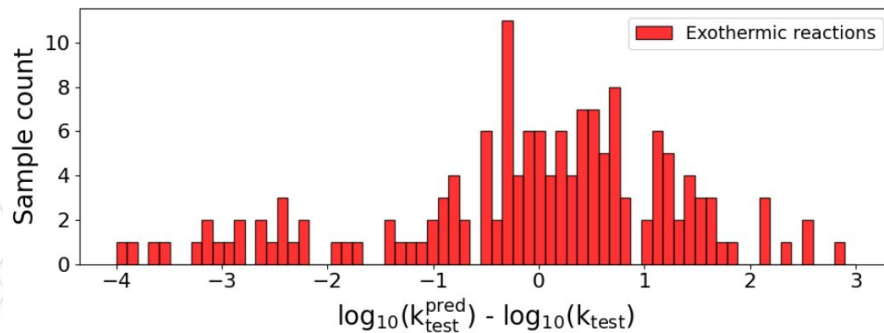
$\Delta H > 0$ : 274 test reactions



Mean Absolute Error on test data: 1.15



Mean Absolute Error on test data: 1.17



# Using the rate coefficient estimator

← → ↻ <https://www.quantemoldb.com/reactions/rate/> ☆

QUANTEMOL GLOBAL MODEL

REACTIONS

SEARCH  
DATA SOURCES  
UPLOAD  
PROCESSES  
DOWNLOAD LIMITS  
API  
DATA CONTRIBUTORS  
CONTRIBUTE DATA

## Rate Coefficient Calculator


Please enter the chemical reaction that you wish to investigate. Please note:

- Elements are case-sensitive, e.g. ArO,CH4,HCL
- Ions are specified by + or -, eventually followed by the charge number, e.g. H+,Cl-,Ar+2
- Species are separated by '+' and reactants and products are separated by '->'
- Reaction rate coefficient only works for two reactant-product pairs e.g. Ar+ + H2O -> Ar + H2O+

Reaction:

Species	Enthalpy (kJ/mol)	Neutral Enthalpy (kJ/mol)	Dipole Moment (D)	Polarizability (Å³)
CH4	-74.6	-74.6	0.0	2.448
O	249.175	249.175	0.0	0.802
CH3	146.9	146.9	0.0	1.835
OH	37.3	37.3	1.66	0.761

The rate coefficient is estimated to be  $7.46 \times 10^{-12} \text{ cm}^3/\text{s}$ .

 QDB is the Quantemol database of species, reactions and chemistries for use in plasma simulations developed by Quantemol.  
For more information, contact us through [this form](#) or at [sales@quantemol.com](mailto:sales@quantemol.com) [Terms of Use and Privacy Policy](#)

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



Filling the gap

# Branching Ratios

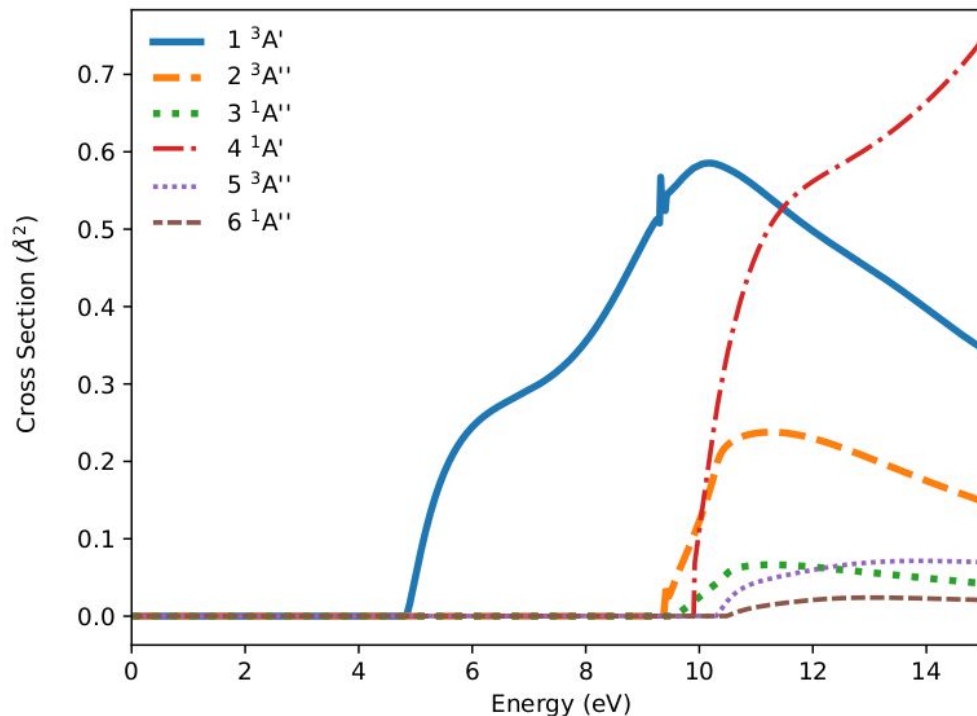


# Electron collisions

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

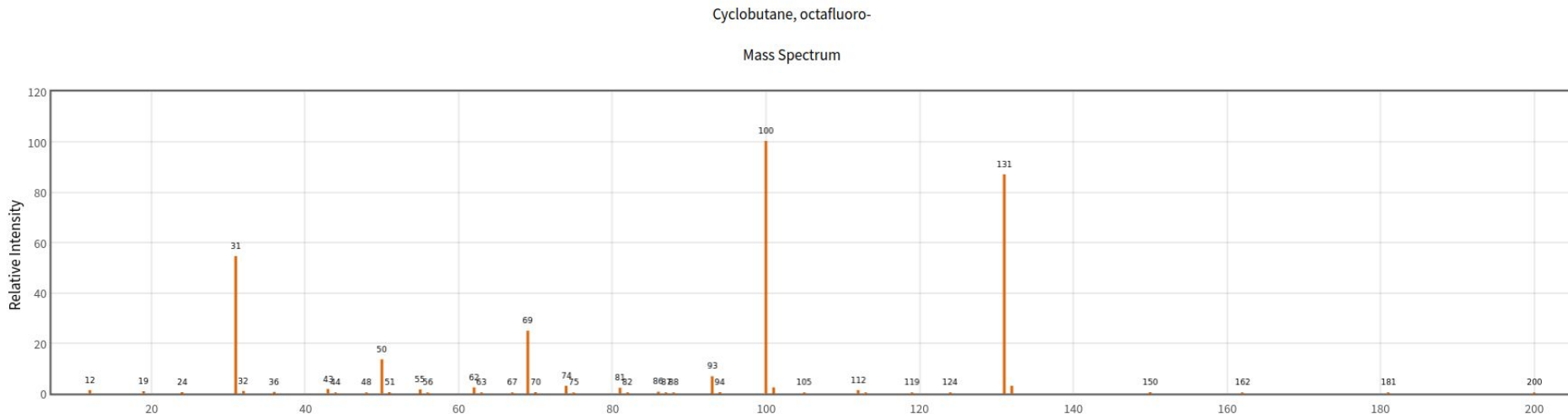
For ionization and dissociation, these calculations do not yield the fragmentation patterns!

Electronic Excitation for  $\text{C}_3\text{H}_2\text{F}_4$



# How to determine fragments - Dissociative Ionization

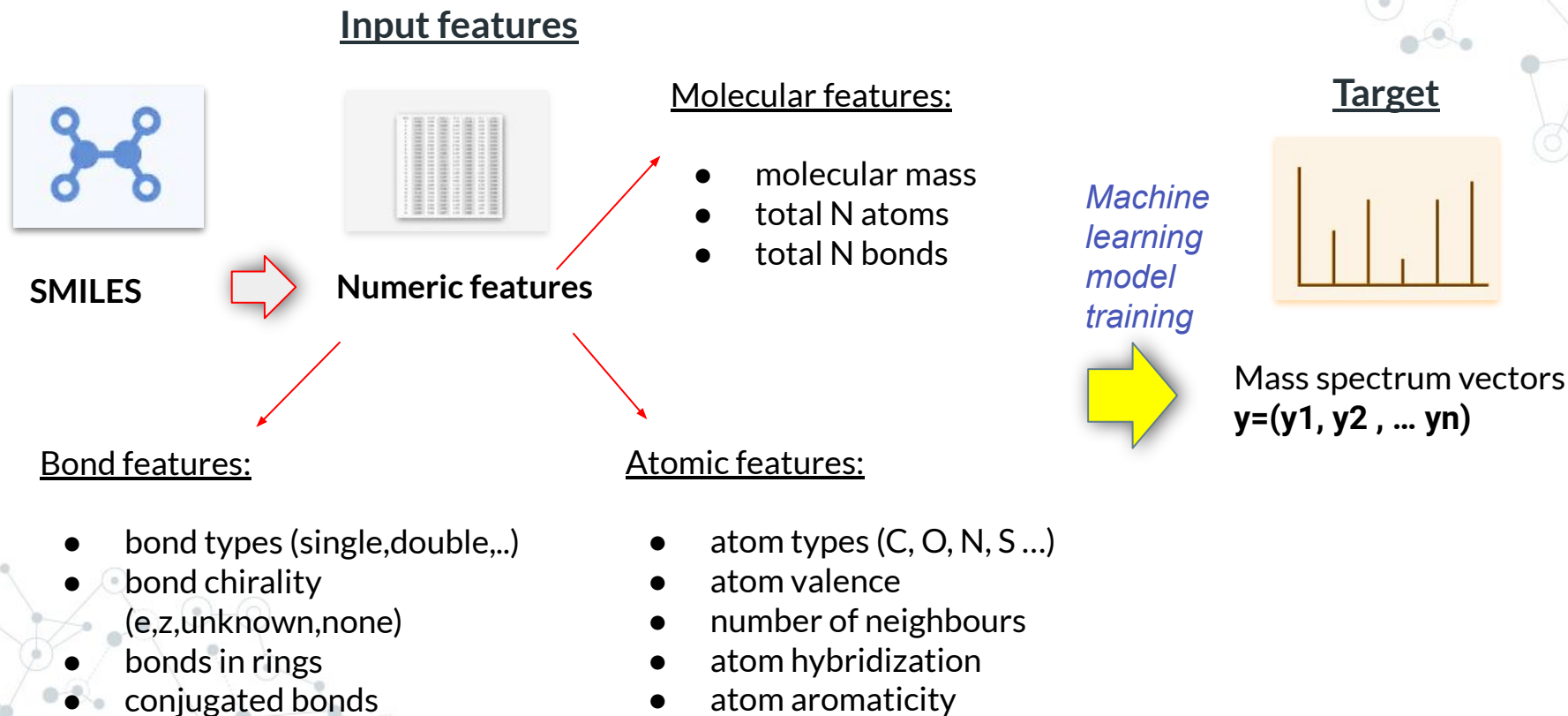
- Mass spectra in combination with bond strengths/appearance potentials can be used to split up the total ionization



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

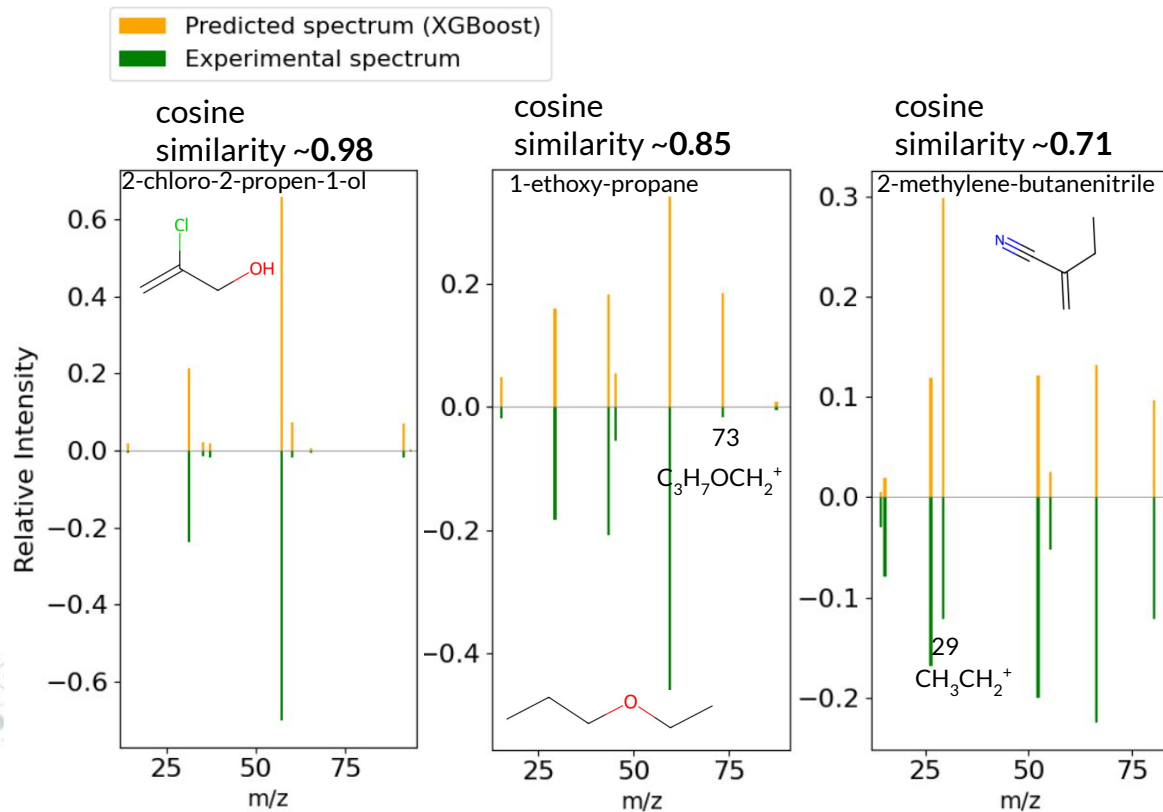


# Prediction of electron impact ionisation fragmentation patterns

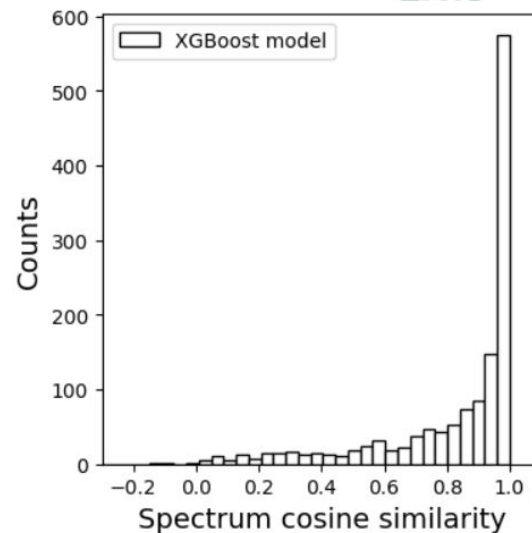


# Prediction of electron impact ionisation fragmentation patterns

Evaluation metric: cosine similarity between real and predicted mass spectra



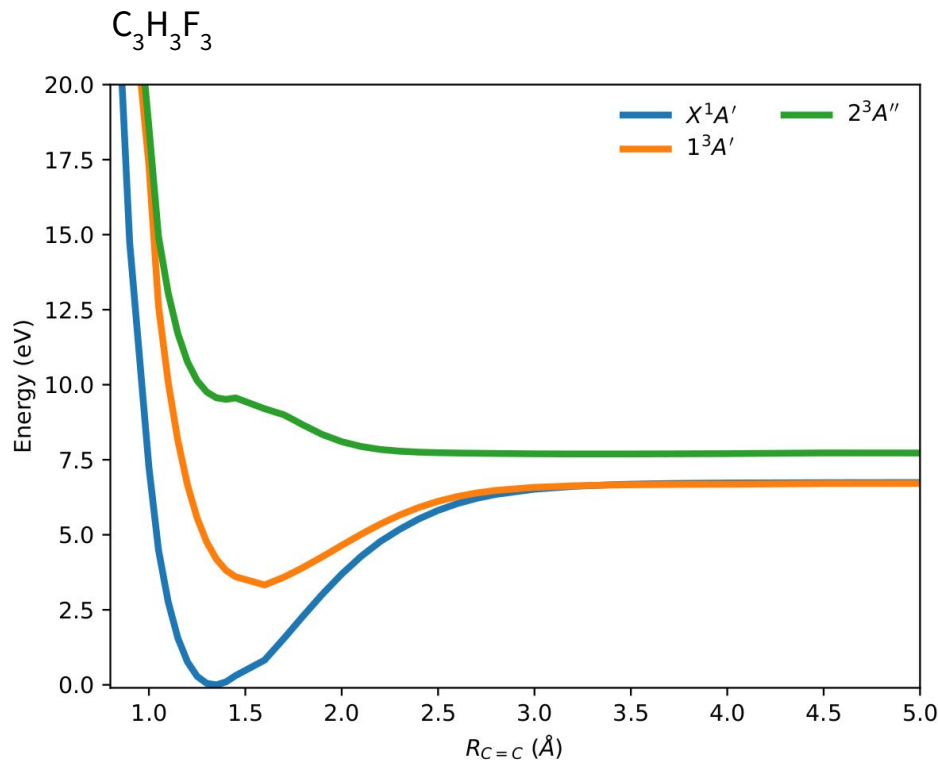
The best performing model so far



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.

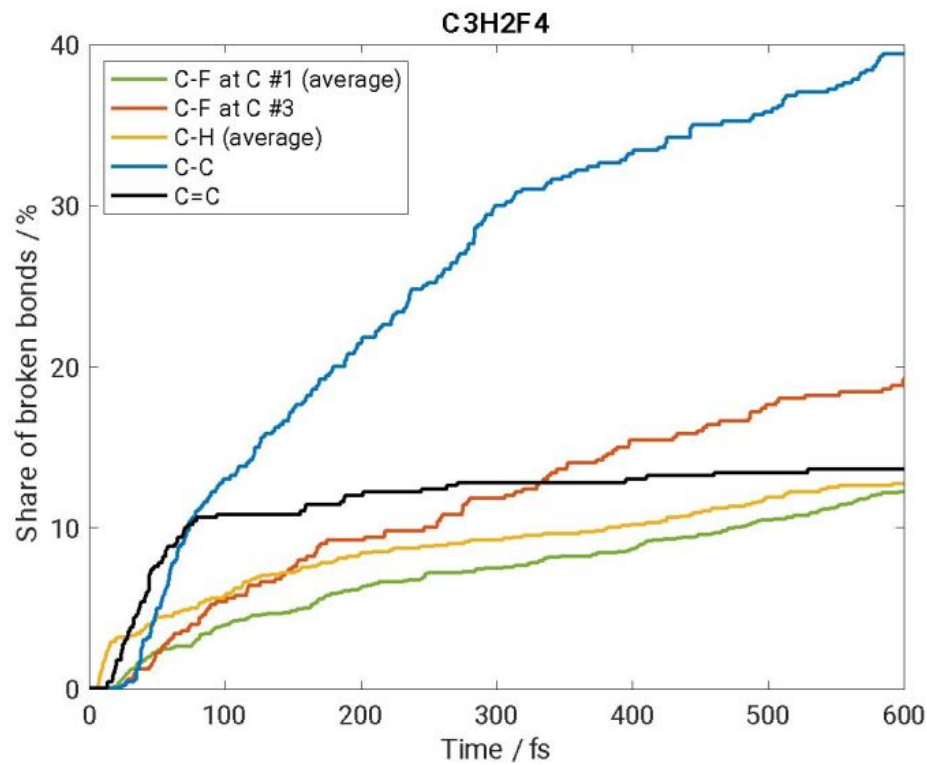


# Explanation

- 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.



# Results for $\text{C}_3\text{H}_2\text{F}_4$



Product	<i>P</i>
F	0.49
CF <sub>3</sub>	0.36
C <sub>2</sub> H <sub>2</sub> F	0.25
H	0.22
C <sub>3</sub> H <sub>2</sub> F <sub>3</sub>	0.20
CHF	0.13

# Summary and Outlook



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.