UCL Department of Physics and Astronomy

Simulating vibrational emission spectra fo low-temperature plasma: Combining QDB and Exocross

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Outline

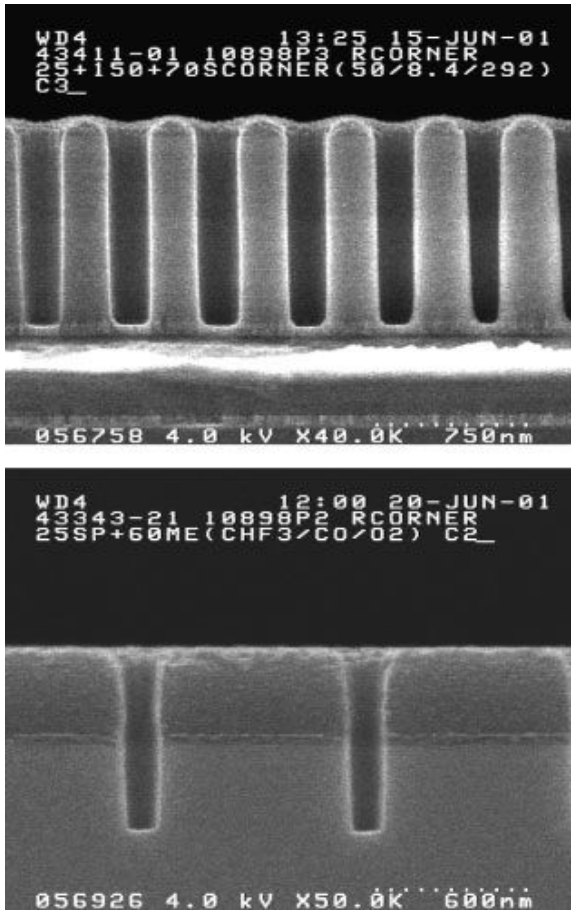
- Introduction: Why we simulate the spectra for plasma?
- Methods: QDB, Pygmol, LiDA, and Exocross
- Results and discussion: species distributions and emission spectra
- Conclusion and outlook

Introduction

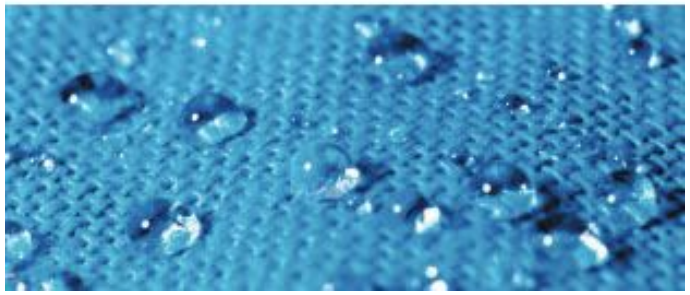
- Plasma is important for almost all the industrial activities, such as
  - Semiconductor chips manufacture
  - Nuclear fusion

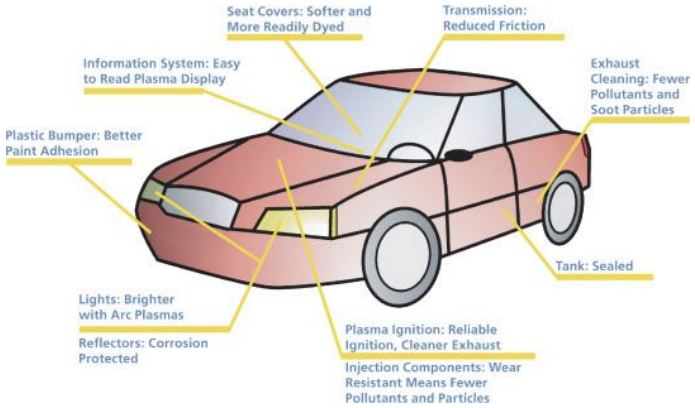
- However, a universal and comprehensive modelling for the dynamics of the chemistry in the plasma is still rare.

- Mainly due to the complex nature of plasma, e.g., for CO_2, 73 species, more than 5000 reactions.



plasma-assisted ‘‘reactive-ion etching’’





Plasma-enhanced chemical vapor deposition

R. d’Agostino, et al. Plasma Process. Polym. 2005, 2, 7–15.

Methods: QDB and PyGmol

- Quantemol data for species and reactions.
- Global model for plasma chemistry.

Species and State	Number of processes		Mass (amu)	Ionization Potential (eV)	Polarizability (Å^3)	Lennard-Jones Radius (Å)	Lennard-Jones Well Depth (K)	State Energy (eV)
	as reactant	as product						
CO_2	231	100	44.010	13.778	2.507	3.940	195.200	N/A
CO_2 v=1	0	1	44.010	13.678	N/A	N/A	N/A	0.100
CO_2 v=2	0	1	44.010	13.603	N/A	N/A	N/A	0.175
CO_2 v=3	0	1	44.010	13.603	N/A	N/A	N/A	0.175
CO_2 v=4	0	1	44.010	11.253	N/A	N/A	N/A	2.525
CO_2 v=5	0	1	44.010	12.253	N/A	N/A	N/A	1.525

Reaction	Process	Data available	
		Cross section	Rate constant data
$e^- + CO_2 \rightarrow O^- + CO$	EDA	✔	–
$CO_2 + CO^+ \rightarrow CO_2^+ + CO$	HIR	–	✔
$O_2 + CO_2^+ \rightarrow O_2^+ + CO_2$	HIR	–	✔
$O + CO_2^+ \rightarrow O^+ + CO_2$	HIR	–	✔
$O + COF \rightarrow CO_2 + F$	HIR	–	✔
$O^* + COF_2 \rightarrow F_2 + CO_2$	HIR	–	✔
$O^* + COF \rightarrow CO_2 + F$	HIR	–	✔

Quantemol Global Model Manual 2022

Release version 1.2
Author: Dr S. Mohr

QDB plasma chemistry

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \left(\frac{\delta n_i}{\delta t}\right)_{\mathrm{vol}} + \left(\frac{\delta n_i}{\delta t}\right)_{\mathrm{flow}} + \left(\frac{\delta n_i}{\delta t}\right)_{\mathrm{diff}}.$$

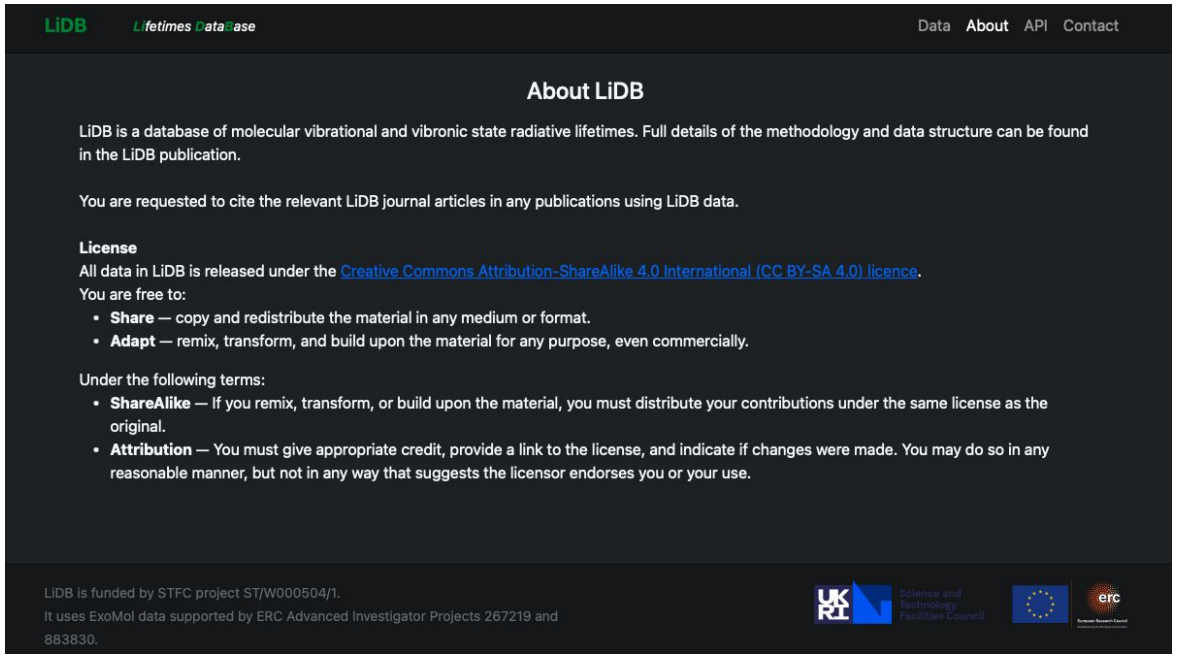
$$\frac{\mathrm{d}\varrho_\mathrm{e}}{\mathrm{d}t} = \frac{P}{V\mathrm{e}} - \left(\frac{\delta \varrho_\mathrm{e}}{\delta t}\right)_{\mathrm{el/inel}} - \left(\frac{\delta \varrho_\mathrm{e}}{\delta t}\right)_{\mathrm{gen/loss}} - \left(\frac{\delta \varrho_\mathrm{e}}{\delta t}\right)_{\mathrm{el\rightarrow walls}} - \left(\frac{\delta \varrho_\mathrm{e}}{\delta t}\right)_{\mathrm{ion\rightarrow walls}}$$

Particle and electron densities dynamics

Hanicinec et al 2020 Plasma Sources Sci. Technol. 29 125024. Tennyson et al 2022 Plasma Sources Sci. Technol. 31 095020

Methods: LiDB (lifetime database)

LiDB is a database of molecular vibrational and vibronic state radiative lifetimes. Full details of the methodology and data structure can be found in the LiDB publication.



States of CO_2

Search:

Vibrational state: (v_1, v_2, v_3)	Energy (eV)	Lifetime (s)	Transitions from	Transitions to
(0, 0, 0)	0.000	∞		7
(0, 0, 1)	0.291	2.38e-03	3	9
(0, 0, 2)	0.579	1.24e-03	5	3
(0, 0, 3)	0.865	8.59e-04	5	2
(0, 0, 4)	1.146	6.69e-04	5	1
(0, 0, 5)	1.180	8.69e-04	5	

Transitions of CO_2

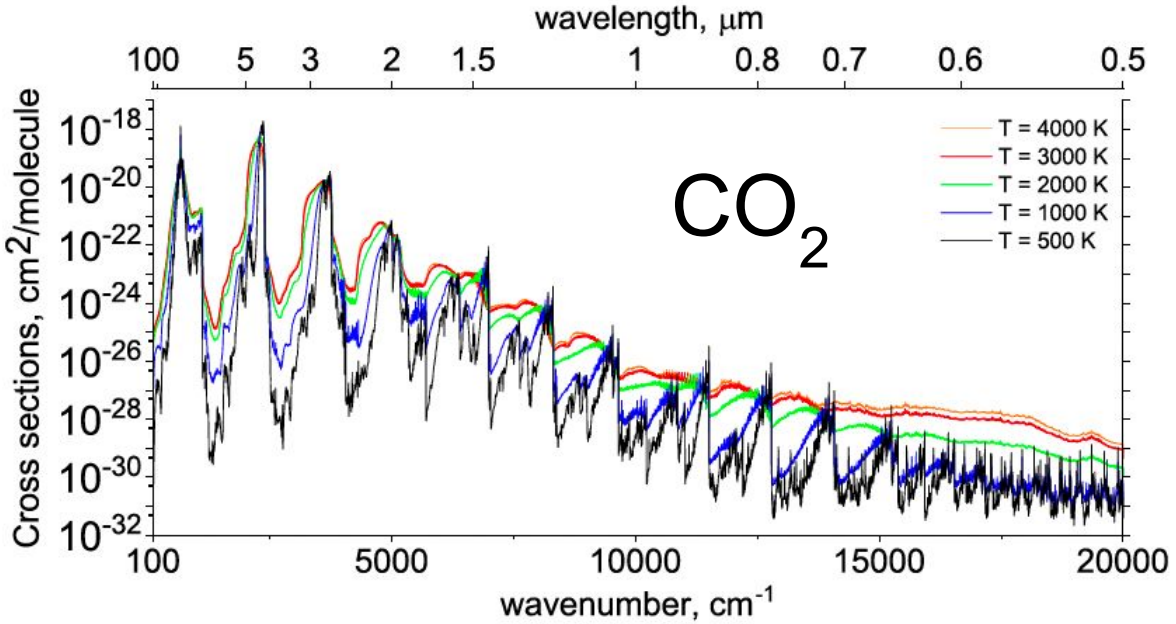
Search:

Initial state	Final state	Δ*E* (eV)	Partial lifetime (s)
v=(0, 0, 1)	*v*=(0, 0, 0)	-0.291	2.38e-03
v=(0, 0, 1)	*v*=(0, 2, 0)	-0.132	2.25e+00
v=(0, 0, 1)	*v*=(1, 0, 0)	-0.119	2.68e+00
v=(0, 0, 2)	*v*=(0, 0, 1)	-0.288	1.24e-03
v=(0, 0, 2)	*v*=(0, 1, 0)	-0.497	7.97e+02
v=(0, 0, 2)	*v*=(0, 2, 1)	-0.131	1.22e+00

Tennyson, et al. Journal of Quantitative Spectroscopy & Radiative Transfer 255 (2020) 107228

Methods: Exocross

- EXOCROSS: a general program for generating spectra from molecular line lists.
- Cross sections, absorption spectra, emission spectra, etc.



$$\epsilon(i \to f) = \frac{g_i^{\text{tot}} A_{fi} \tilde{\nu}_{fi}}{4\pi} \frac{e^{-c_2 \tilde{E}_i/T}}{Q(T)}.$$

Table 5. Extract from the states file of the $^{14}N^{16}O$ line list.

i	Energy (cm^{-1})	g_i	J	τ	g_J	+/−	e/f	State	v	Λ	Σ	Ω
1	0.000000	6	0.5	inf	−0.000767	+	e	X1/2	0	1	−0.5	0.5
2	1876.076228	6	0.5	8.31E−02	−0.000767	+	e	X1/2	1	1	−0.5	0.5
3	3724.066346	6	0.5	4.25E−02	−0.000767	+	e	X1/2	2	1	−0.5	0.5
4	5544.020643	6	0.5	2.89E−02	−0.000767	+	e	X1/2	3	1	−0.5	0.5
5	7335.982597	6	0.5	2.22E−02	−0.000767	+	e	X1/2	4	1	−0.5	0.5
6	9099.987046	6	0.5	1.81E−02	−0.000767	+	e	X1/2	5	1	−0.5	0.5
7	10 836.058173	6	0.5	1.54E−02	−0.000767	+	e	X1/2	6	1	−0.5	0.5
8	12 544.207270	6	0.5	1.35E−02	−0.000767	+	e	X1/2	7	1	−0.5	0.5
9	14 224.430238	6	0.5	1.21E−02	−0.000767	+	e	X1/2	8	1	−0.5	0.5
10	15 876.704811	6	0.5	1.10E−02	−0.000767	+	e	X1/2	9	1	−0.5	0.5
11	17 500.987446	6	0.5	1.01E−02	−0.000767	+	e	X1/2	10	1	−0.5	0.5
12	19 097.209871	6	0.5	9.41E−03	−0.000767	+	e	X1/2	11	1	−0.5	0.5
13	20 665.275246	6	0.5	8.83E−03	−0.000767	+	e	X1/2	12	1	−0.5	0.5
14	22 205.053904	6	0.5	8.35E−03	−0.000767	+	e	X1/2	13	1	−0.5	0.5
15	23 716.378643	6	0.5	7.94E−03	−0.000767	+	e	X1/2	14	1	−0.5	0.5
16	25 199.039545	6	0.5	7.59E−03	−0.000767	+	e	X1/2	15	1	−0.5	0.5

Yurchenko, et al., Astronomy & Astrophysics, 614, A131 (2018)

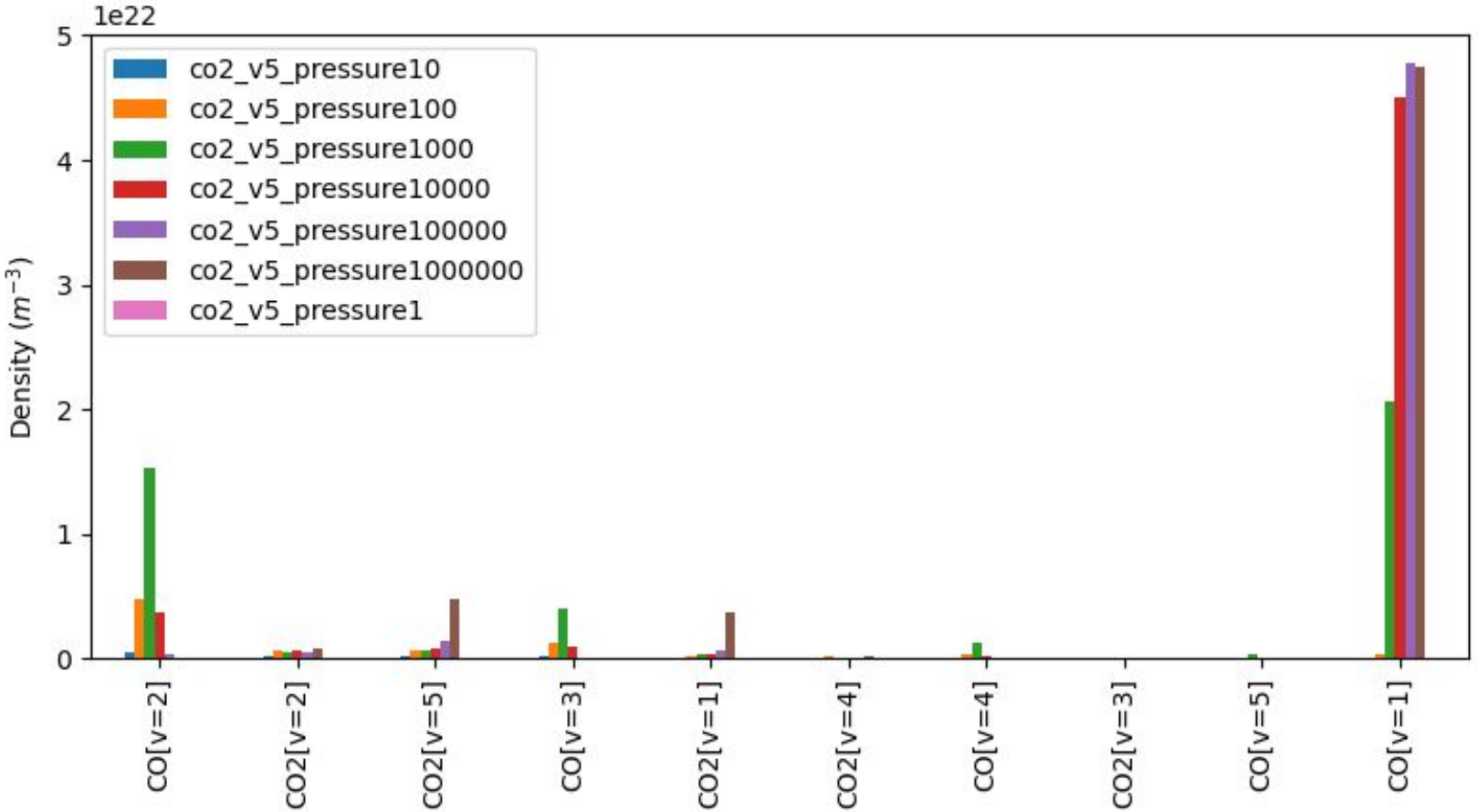
Methods: integration

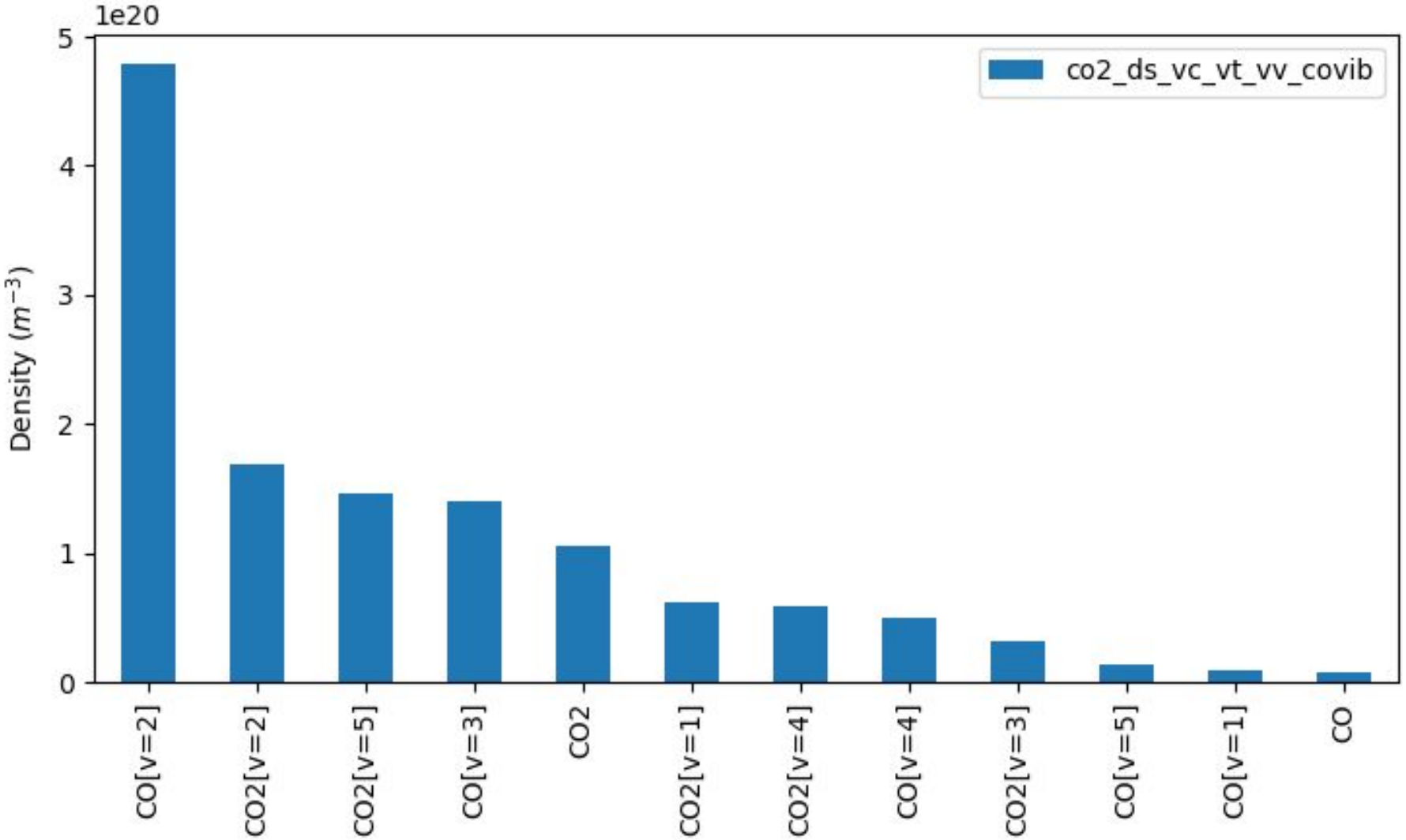
- Add decay of vibrational excited states.
- Add heavy particle collision for vibrational excited states, using the data in the STELLAR database.
- Integrate QDB and LiDB data into Pygmol plasma chemistry simulations and obtain the species distributions.
- Compute emission spectra using Pyexocross (python version of ExoCross).

Vargas, et al. J. Phys. Chem. A 2021, 125, 2, 493–512

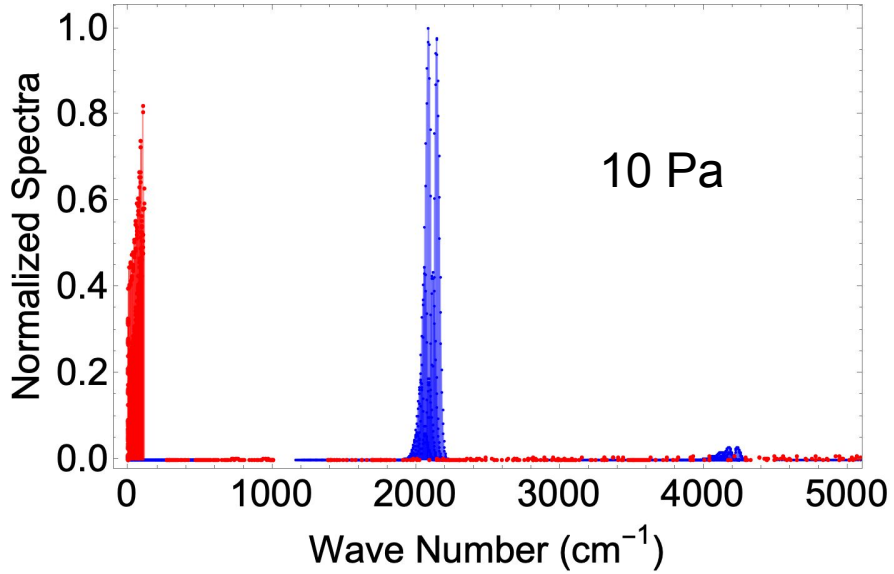
Database: http://esther.ist.utl.pt/pages/stellar.html

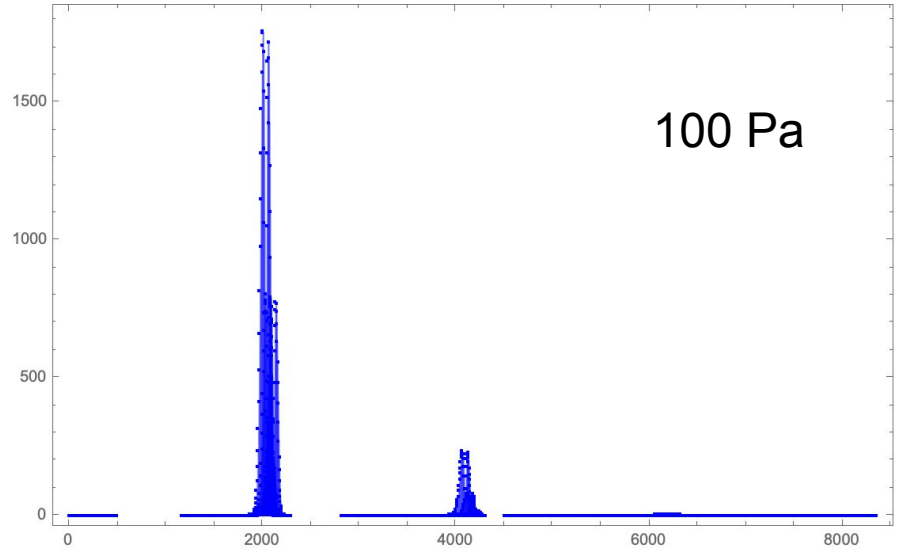
Results: population distributions (CO_2)

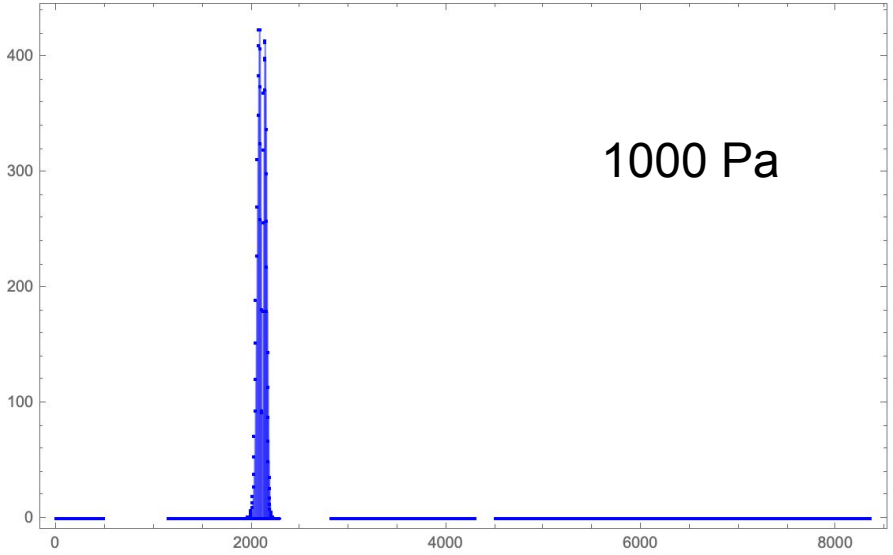


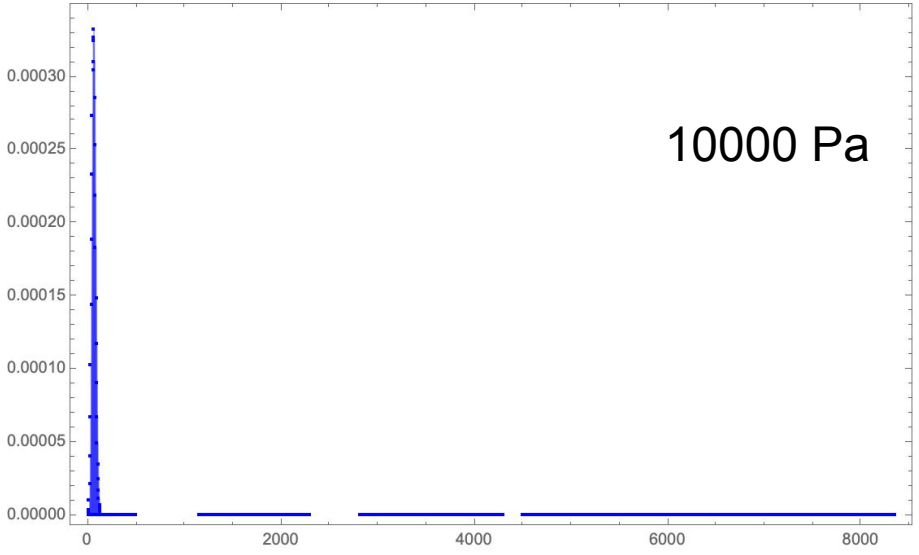

1e20
5
4
3
2
1
0
Density (m^{-3})
co2_ds_vc_vt_vv_covib
CO[v=2]
CO2[v=2]
CO2[v=5]
CO[v=3]
CO2
CO2[v=1]
CO2[v=4]
CO[v=4]
CO2[v=3]
CO[v=5]
CO[v=1]
CO

Results: Pressure- dependent CO_2 plasma emission spectra

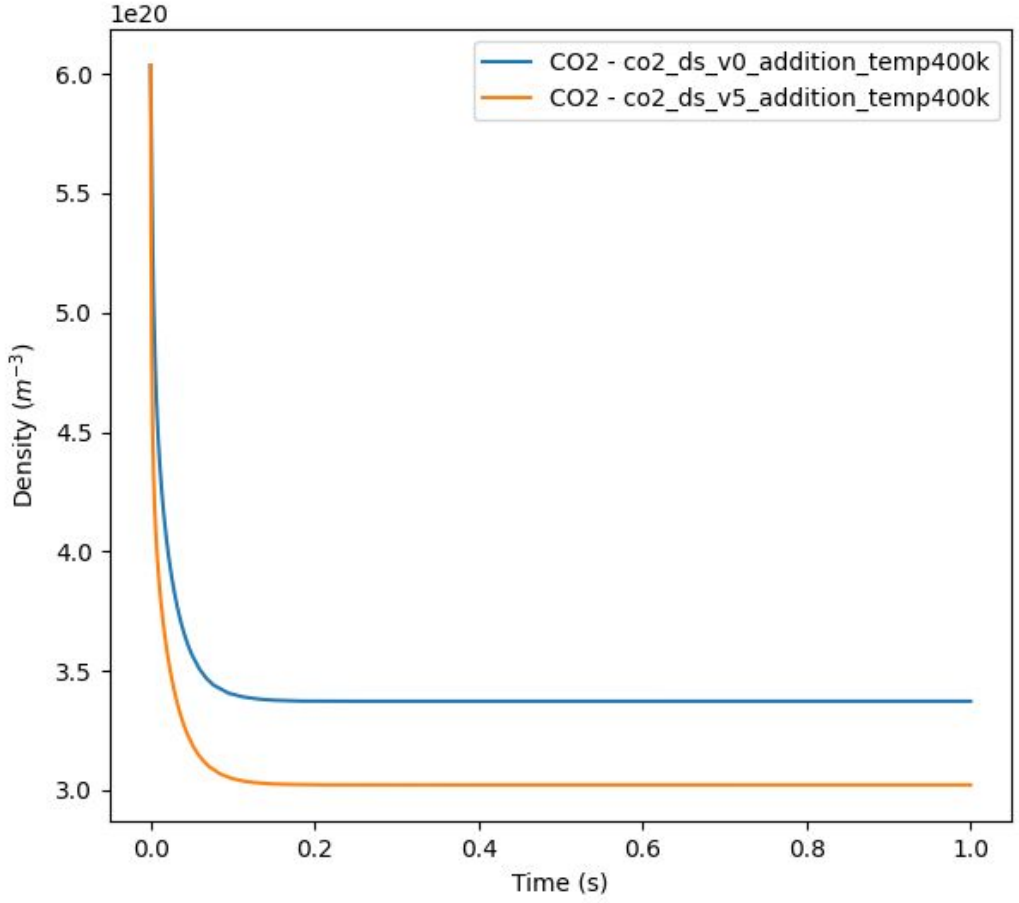


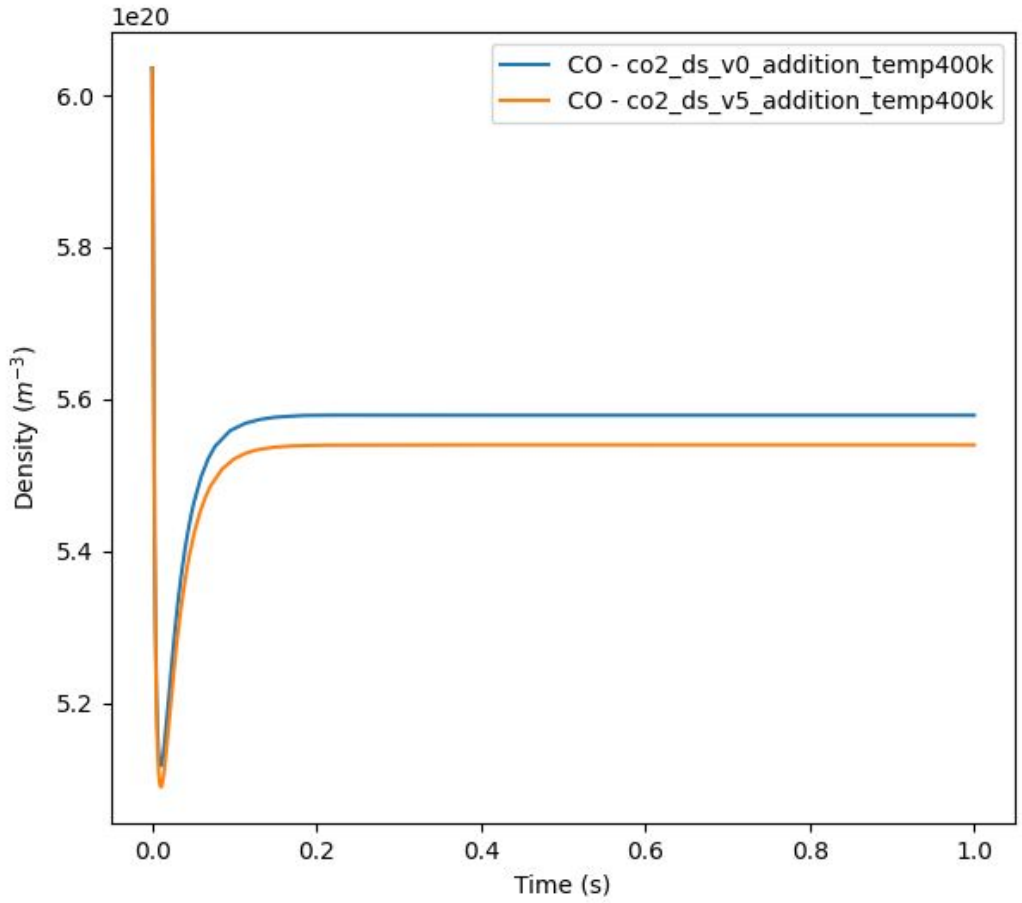






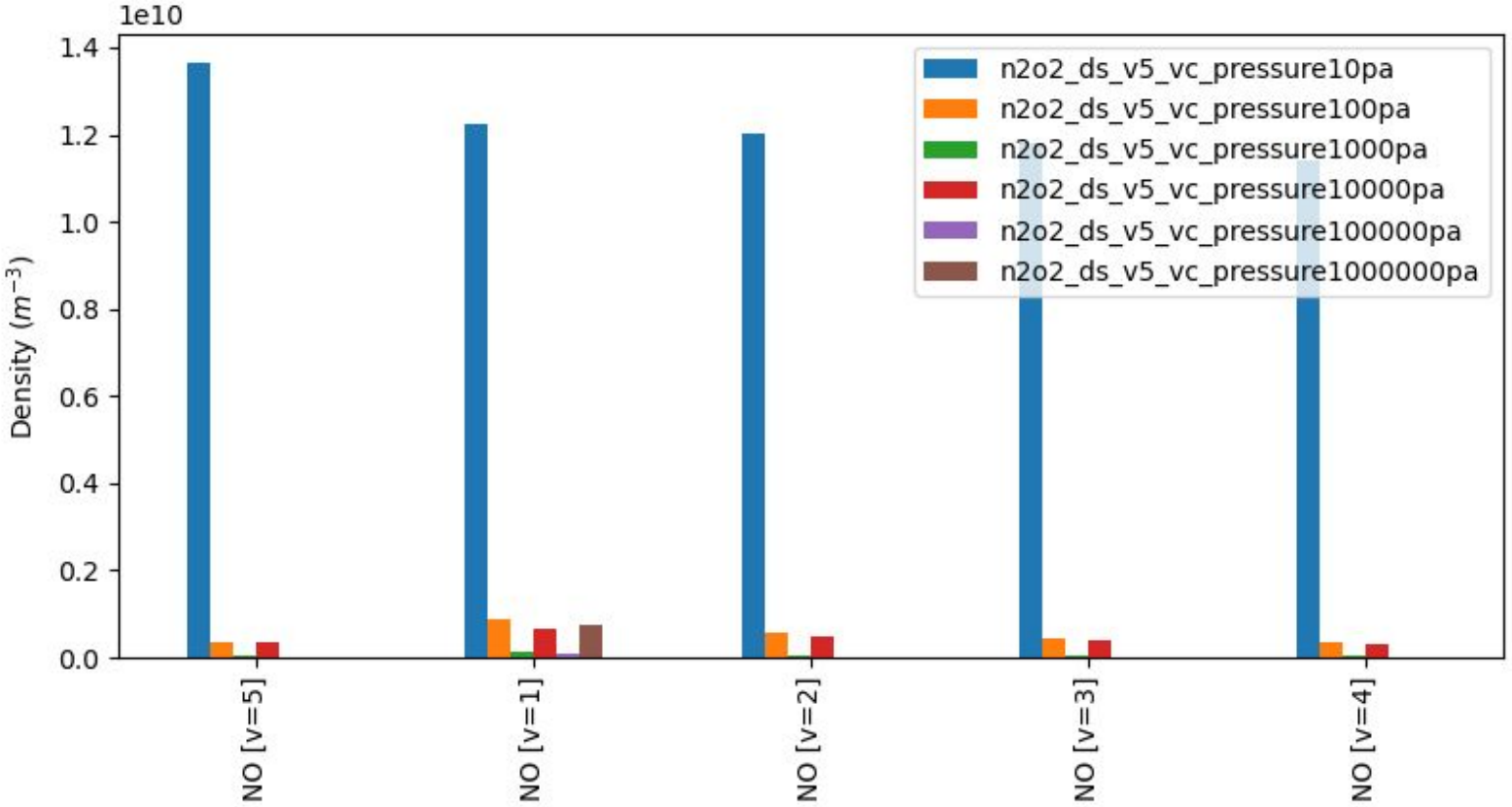
Results: time dependence



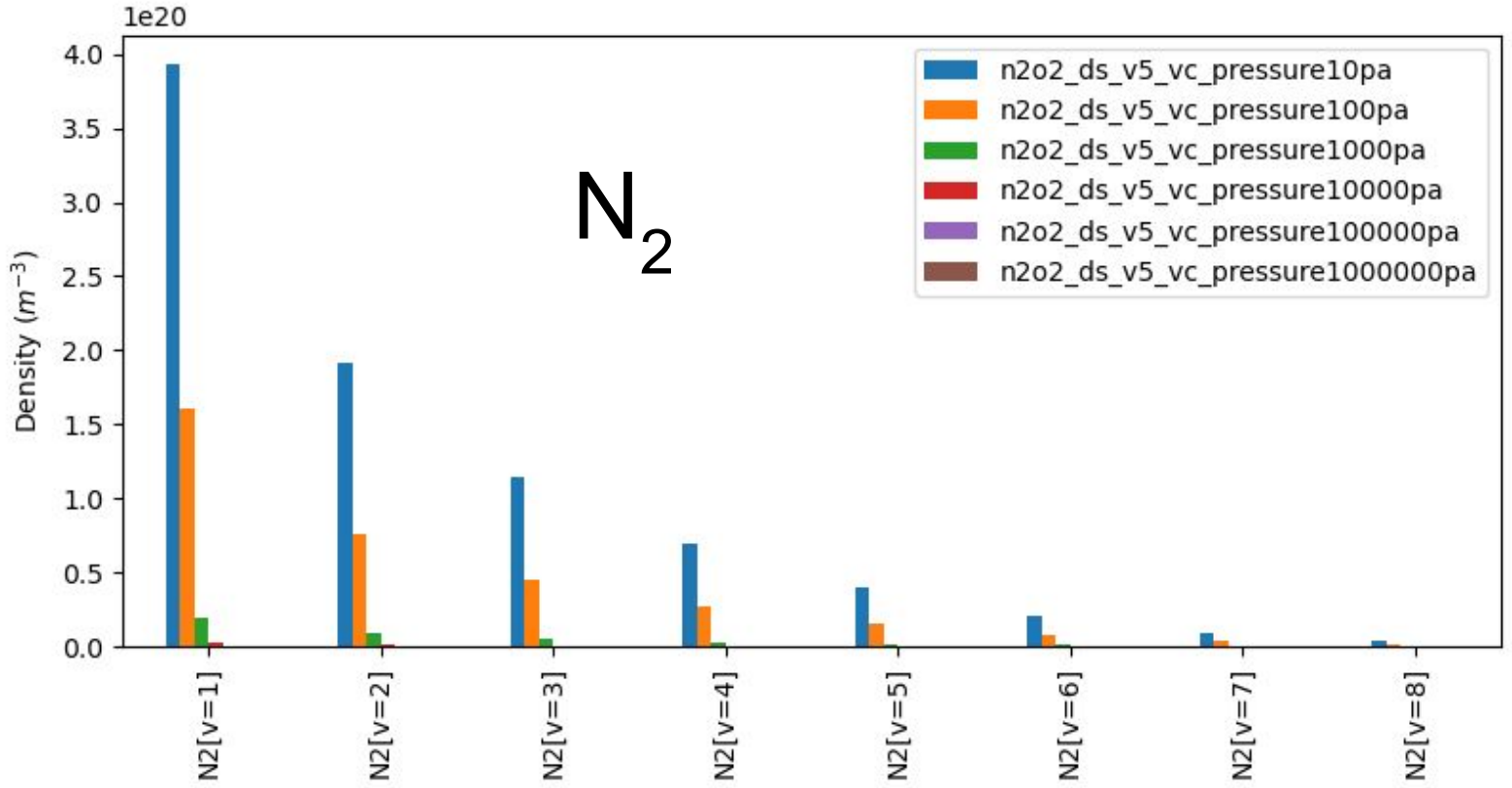


Results: $N_2 + O_2$

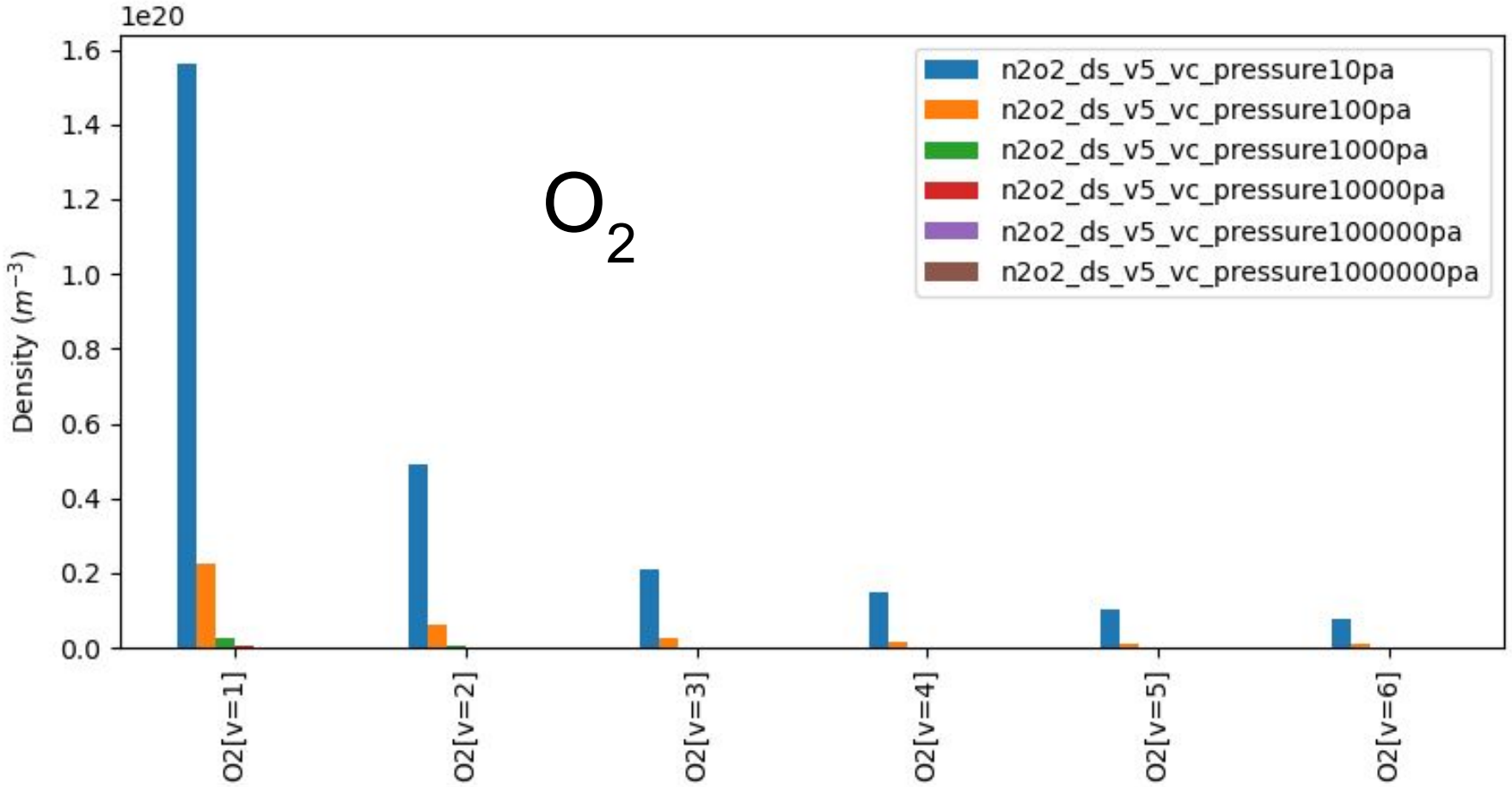
NO



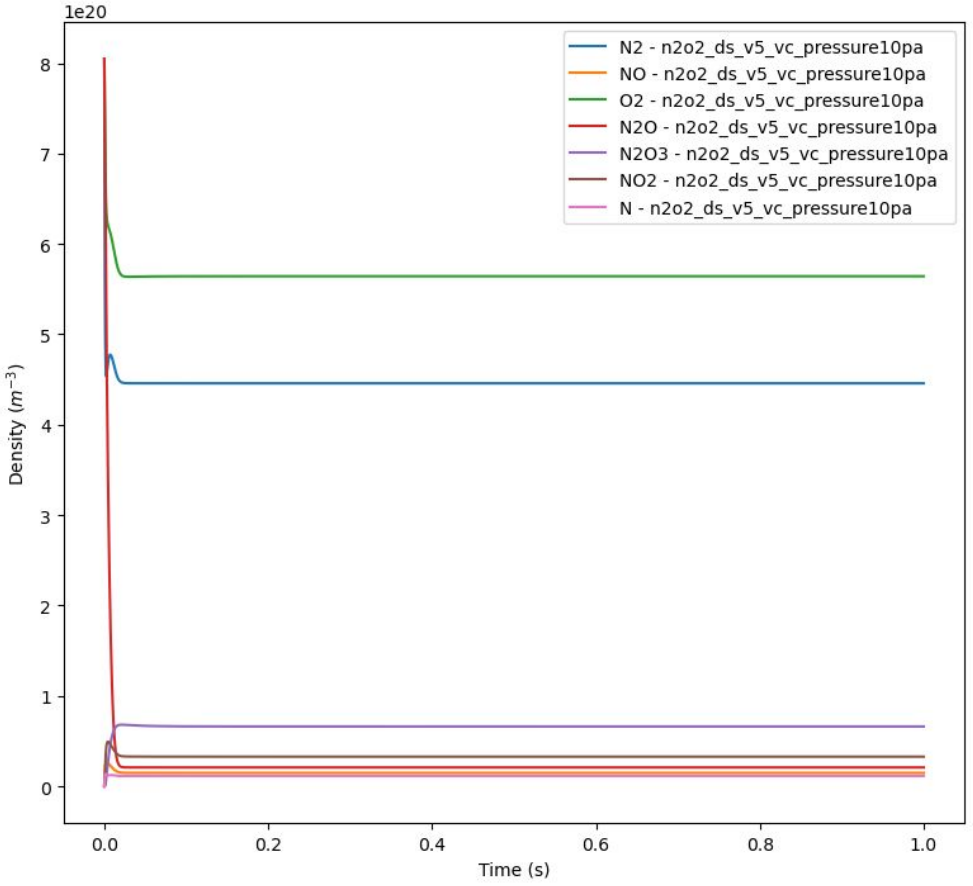
Results: $N_2 + O_2$

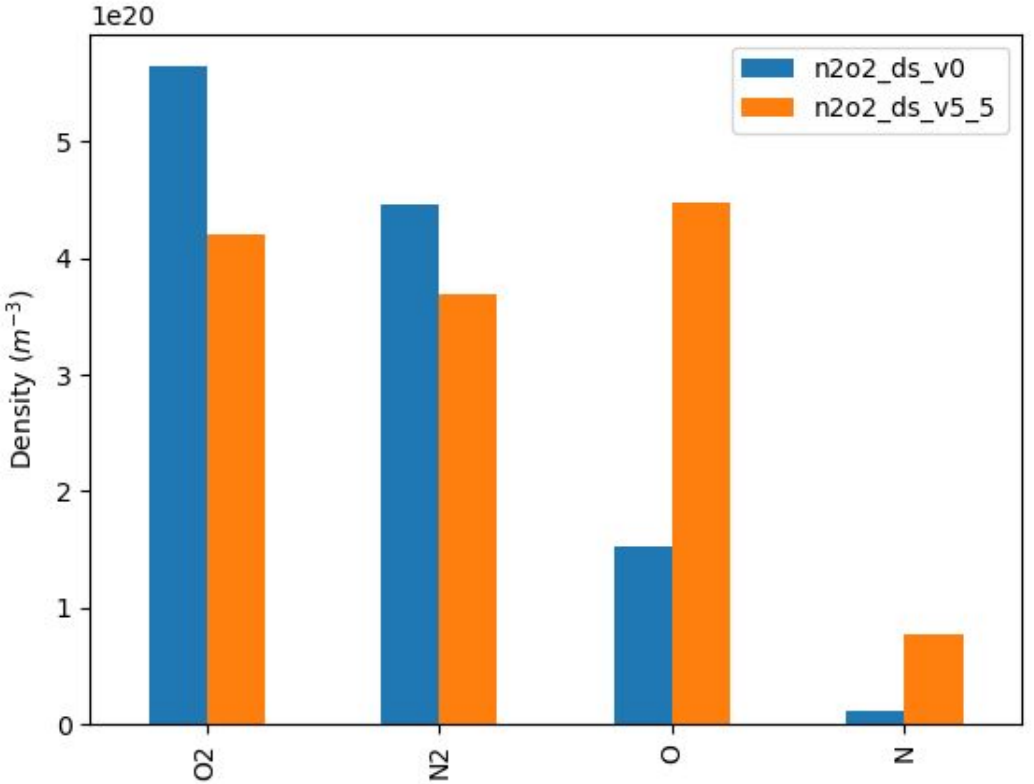


Results: $N_2 + O_2$



Results: $N_2 + O_2$





Conclusion and outlook

- ✔ Computed emission spectra by integrating QDB, LiDB, Pygmol, and Exocross.
- ✔ Obtained the species distributions from QDB App.
- ✔ Clearly see the CO_2 and CO spectra lines.
- ☐ Finish the spectra calculations for CO_2 and publication.
- ☐ Extend methodologies to other interesting systems such as N_2+O_2.
- ☐ Integrate softwares mentioned above into a single Python framework.

Acknowledgement

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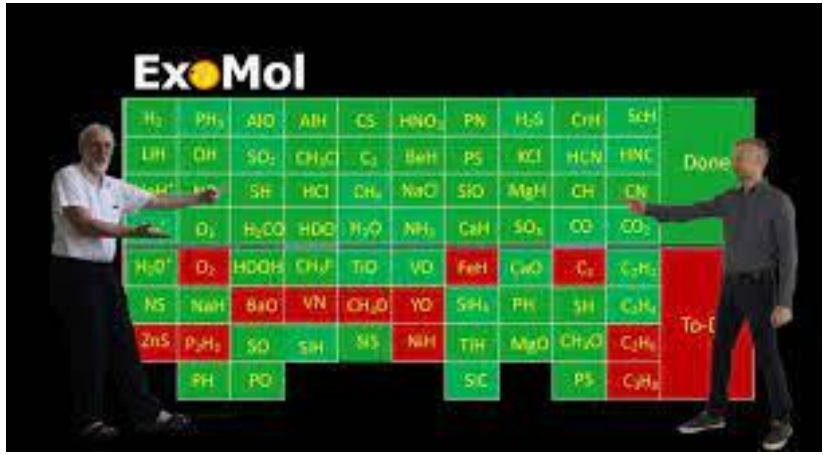

Thank you for listening!