

Self-consistent Fokker-Planck approach to CO₂ vibrational kinetics

P. Viegas¹, M. C. M. van de Sanden¹, S. Longo² and P. Diomedede¹

¹ CPPC group, DIFFER, Eindhoven, the Netherlands

² Dipartimento di Chimica, Bari, Italy

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Motivation - CO₂ conversion

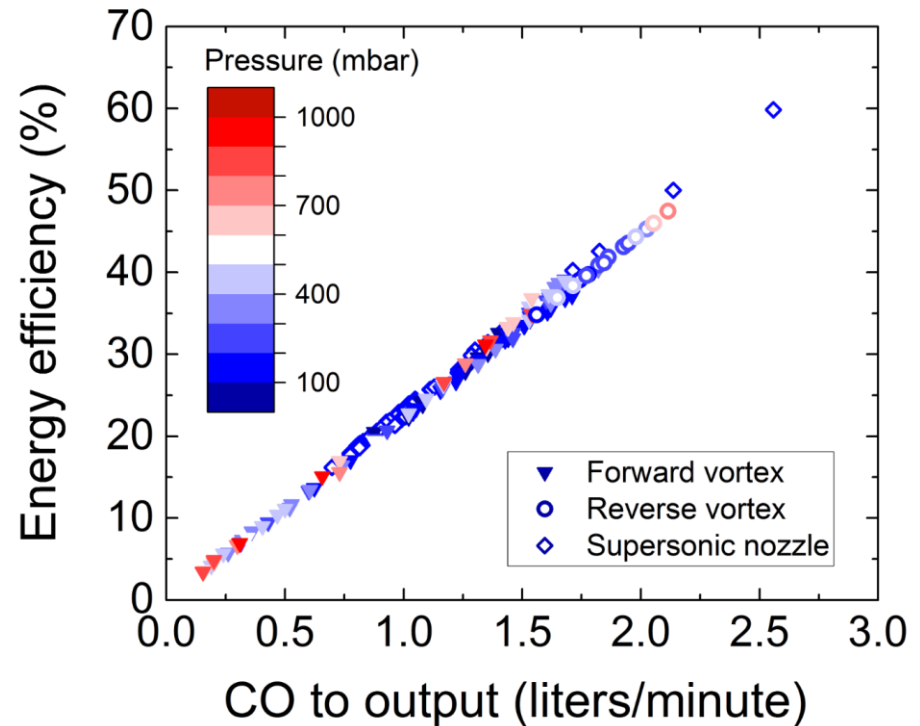
Efficient conversion in plasma reactors at DIFFER:

Forward vortex

Supersonic expansion



Reverse vortex

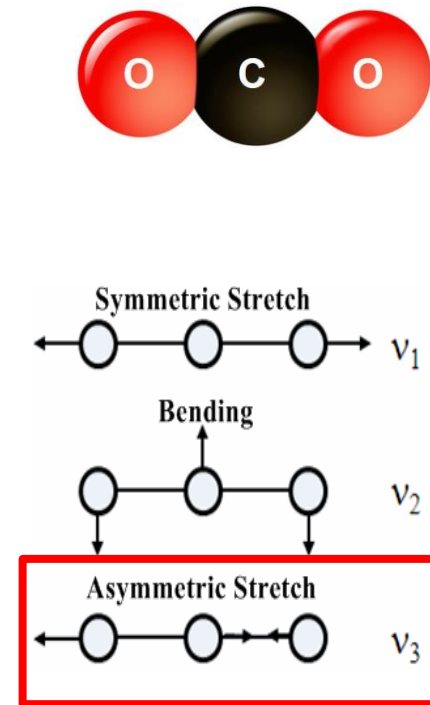
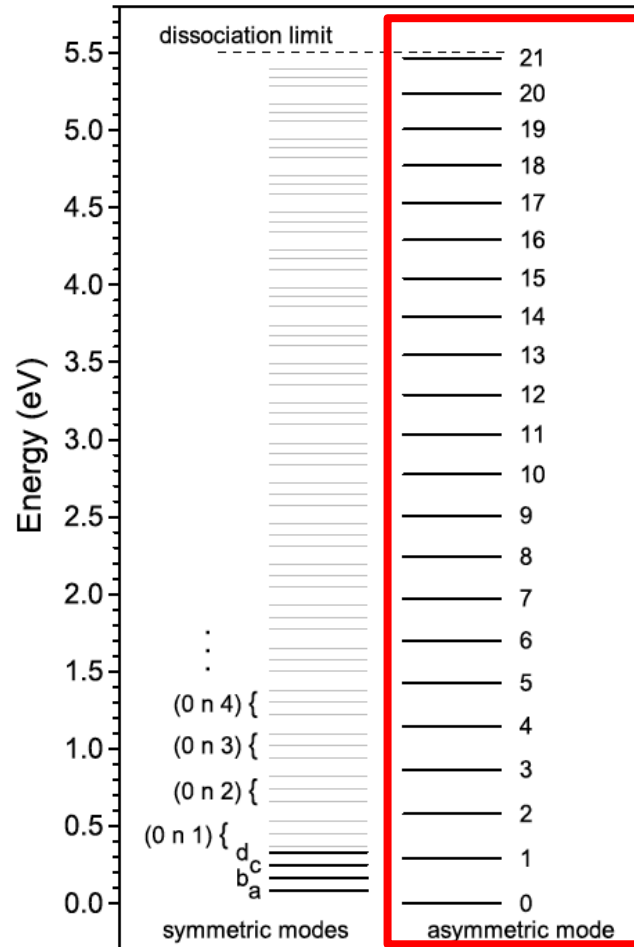


Understanding and optimizing CO₂ conversion in MW plasma reactors requires **multidimensional modelling**



Modelling CO₂ plasma reactors

- The description of plasma reactors requires **multidimensional models** that couple microwave, flow, heat and plasma.
- **Vibrational non-equilibrium** has an impact on dissociation mechanisms in CO₂ discharge reactors.



Kozak and Bogaerts, PSST 2014



Modelling CO₂ plasma reactors

- The description of plasma reactors requires **multidimensional models** that couple microwave, flow, heat and plasma.
- **Vibrational non-equilibrium** has an impact on dissociation mechanisms in CO₂ discharge reactors.
- Usual State-To-State (STS) approach:
Resolution of conservation equations for **dozens of vibrational levels**, including all their **reactions**.
- In reactor models, the STS approach can compromise **computational efficiency**.



Modelling CO₂ plasma reactors

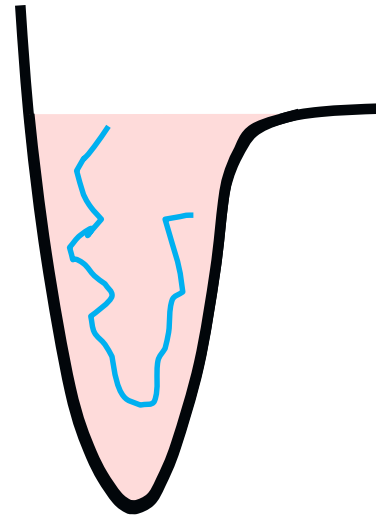
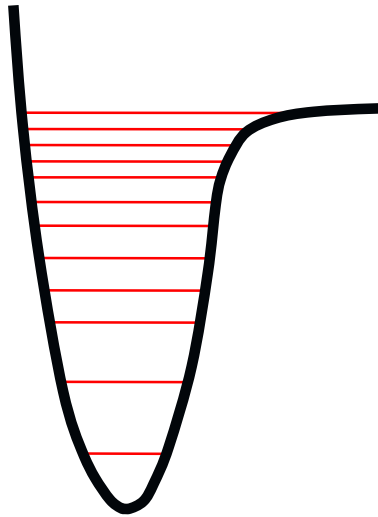
- Alternatively, we can consider only a few species and **effective rate coefficients** that take into account **vibrational non-equilibrium**
- But it still requires the population of vibrationally excited states:
Vibrational Distribution Function (VDF)
- Need **fast solution of the VDF** that can be coupled with plasma models and preserves accurate results



Alternative approach for vibrational kinetics

Multilevel kinetics

→ Brownian motion



Collisional interactions

→ Drift and diffusion in energy space

System of ODEs

→ **Fokker-Planck Equation**



From STS to Fokker-Planck (FP) approach

Gain-loss equation for population of states i :

$$\frac{d n_i}{dt} = \sum_j S_{ij}(t)$$

n_i = number density of species i

S_{ij} = source term associated to reaction j

- Assumption of **continuum in energy space** of asymmetric stretching vibrational mode:
Energy between states \ll dissociation energy
- Assumption of **only small energy transitions**:
Monoquantum transitions

References:

Van Kampen,

North-Holland (1981)

Biberman *et al.*,

Consultants Bureau (1987)



Fokker-Planck (FP) approach

$$\frac{df(\varepsilon)}{dt} = - \frac{dJ(\varepsilon)}{d\varepsilon}$$

$$J(\varepsilon) = A(\varepsilon)f(\varepsilon) - B(\varepsilon) \frac{df(\varepsilon)}{d\varepsilon}$$

f = vibrational distribution function

J = flux in energy space

A = drift coefficient

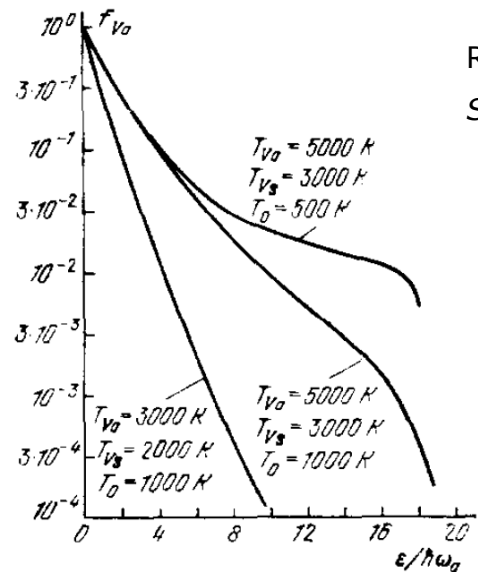
B = diffusion coefficient

Transport coefficients

A and B as $f(T_g, T_v, k)$

derived for each process in

Viegas *et al.*, submitted



Rusanov, Fridman and Sholin,
Sov. Phys. Usp. **24** (1981), 447

FIG. 7. Population of antisymmetric CO₂ vibrational mode.



Numerical FP approach

In **stationary conditions**,

$$\frac{df(\varepsilon)}{dt} = -\frac{dJ}{d\varepsilon} = 0$$

f = vibrational distribution function
 J = flux in energy space

J is uniform and can be defined as
dissociation rate at $\varepsilon = \varepsilon_{diss}$

Finding J and f becomes a flux-matching
problem that can be solved **fast**

**Need to implement in
self-consistent plasma model
and verify its correctness**

Diomedede *et al.*, *J. Phys. Chem. C* **121** (2017), 19568

Diomedede *et al.*, *J. Phys. Chem. A* **122** (2018), 7918



Benchmarking the FP approach

Comparison of STS and FP approaches, assuming:

- Fixed pressure $p = 100$ mbar and gas temperature $T_g = 300$ K.
- Constant input power density P_{dep} .
- **Almost pure CO₂ plasma**; low dissociation.
- Dissociation only through asymmetric stretching vibrational channel.
- Same kinetic data in STS and FP models.



Zero-dimensional STS model

- Electron energy ε_m equation
- Species densities rate equations:

$$\frac{d n_i}{dt} = \sum_j S_{ij}(t)$$

n_i = number density of species i

S_{ij} = source term associated to reaction j

- Solved until **stationary condition** is reached
- $k(\varepsilon_m)$ from EEDF solution from Bolsig+ for pure CO₂
- Kinetic data from
Kozak and Bogaerts, *Plasma Sources Sci. Technol.* **23** (2014), 045004



Zero-dimensional STS model

Total of 261 reactions and **28 ODEs** to solve:

$\epsilon_m, e, \text{CO}_2(v=0-21), \text{CO}_2(v_a), \text{CO}_2(v_b), \text{CO}_2(v_c), \text{CO}_2(v_d)$

1. Ionization: $e + \text{CO}_2(v=0-3, v_a, v_b, v_c) \rightarrow \text{CO}_2^+ + 2 e$
2. Recombination: $e + \text{CO}_2^+ \rightarrow \text{CO}_2 (\text{CO}+\text{O})$
3. e-V: $e + \text{CO}_2(v=0-2, v_a, v_b, v_c) \longleftrightarrow \text{CO}_2(v=1-3, v_a, v_b, v_c) + e$
4. V-V: $\text{CO}_2(v=n) + \text{CO}_2(v=1) \longleftrightarrow \text{CO}_2(v=n+1) + \text{CO}_2(v=0)$
 $\text{CO}_2(v=n) + \text{CO}_2(v=n) \longleftrightarrow \text{CO}_2(v=n+1) + \text{CO}_2(v=n-1)$
5. V-V dissociation: $\text{CO}_2(v=21) + \text{CO}_2(v=1) \rightarrow \text{CO}_2 (\text{CO}+\text{O}) + \text{CO}_2(v=0)$
 $\text{CO}_2(v=21) + \text{CO}_2(v=21) \rightarrow \text{CO}_2 (\text{CO}+\text{O}) + \text{CO}_2(v=20)$
6. V-V': $\text{CO}_2(v=n) + \text{CO}_2(v=0) \longleftrightarrow \text{CO}_2(v=n-1) + \text{CO}_2(v_a, v_b)$
7. V-T: $\text{CO}_2(v=n) + \text{CO}_2 \longleftrightarrow \text{CO}_2(v=n-1) + \text{CO}_2$
 $\text{CO}_2(v_a, v_b, v_c, v_d) + \text{CO}_2 \longleftrightarrow \text{CO}_2(v=0, v_a, v_b, v_c) + \text{CO}_2$



Reduced STS + FP model

- Use a simplified STS model to calculate T_v in stationary condition:
Same energy equation and electron rate equation as full STS model;
V-V, V-V' and V-T in asymmetric stretching mode truncated at $v=3$.
- Total of 77 reactions and 9 ODEs to solve:
 ε_m , e , $\text{CO}_2(v=0-3)$, $\text{CO}_2(v_a)$, $\text{CO}_2(v_b)$, $\text{CO}_2(v_c)$
- Solve the stationary FP equation to obtain the VDF and the V-V dissociation rate.
Replaces STS V-V, V-V' and V-T in asymmetric stretching mode.



Benchmarking the FP approach ($P_{dep} = 1000 \text{ Wcm}^{-3}$)

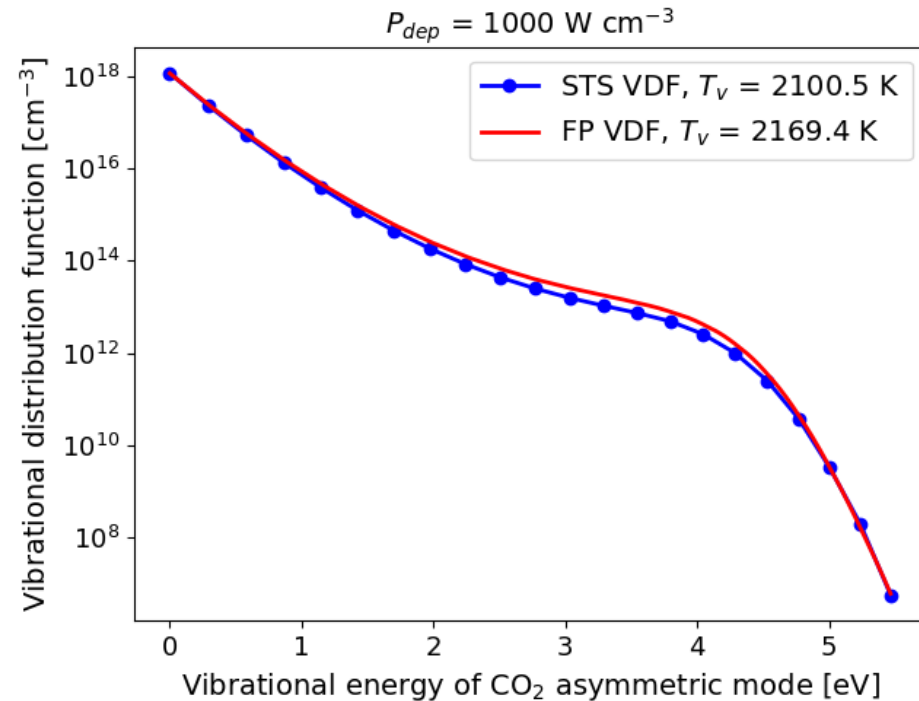
Full STS model:

- $n_e = 1.9 \times 10^{11} \text{ cm}^{-3}$ and $T_e = 1.52 \text{ eV}$
- $T_v = 2101 \text{ K}$
- V-V dissociation rate = $1.11 \times 10^{12} \text{ cm}^{-3}\text{s}^{-1}$
- Calculation time **423.87 s**

Reduced STS + FP model:

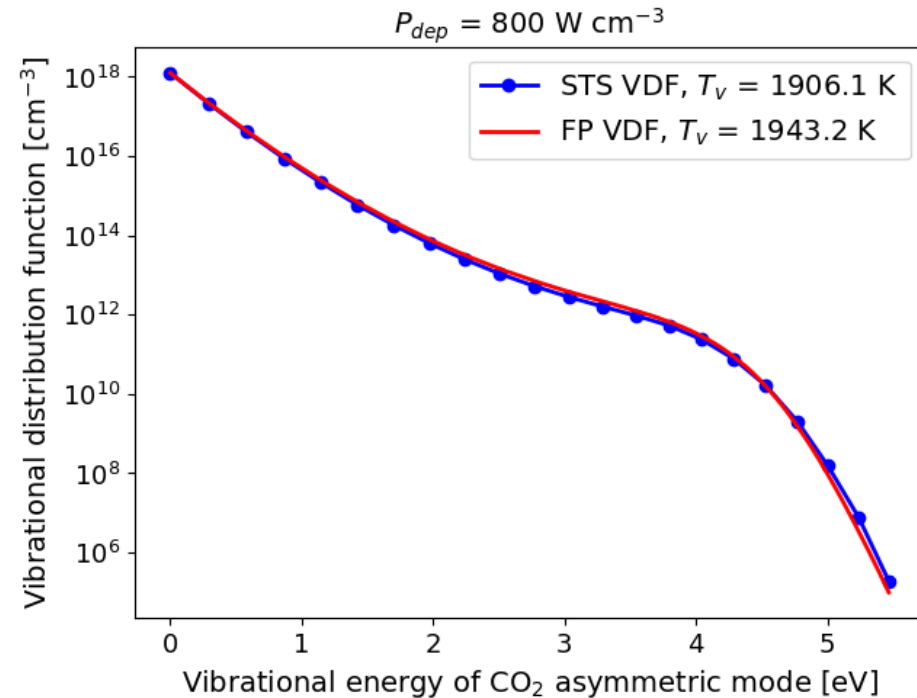
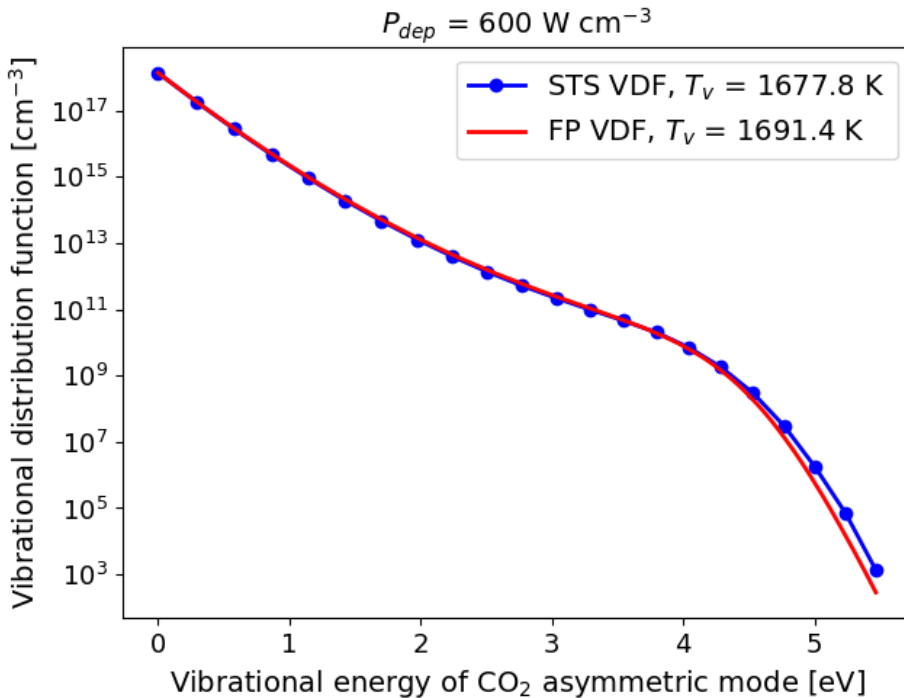
- $n_e = 1.9 \times 10^{11} \text{ cm}^{-3}$ and $T_e = 1.52 \text{ eV}$
- $T_v = 2169 \text{ K}$
- V-V dissociation rate = $1.24 \times 10^{12} \text{ cm}^{-3}\text{s}^{-1}$
- Calculation time **69.61 s** (69.58 + 0.03 s)

- **Very good agreement on VDF**





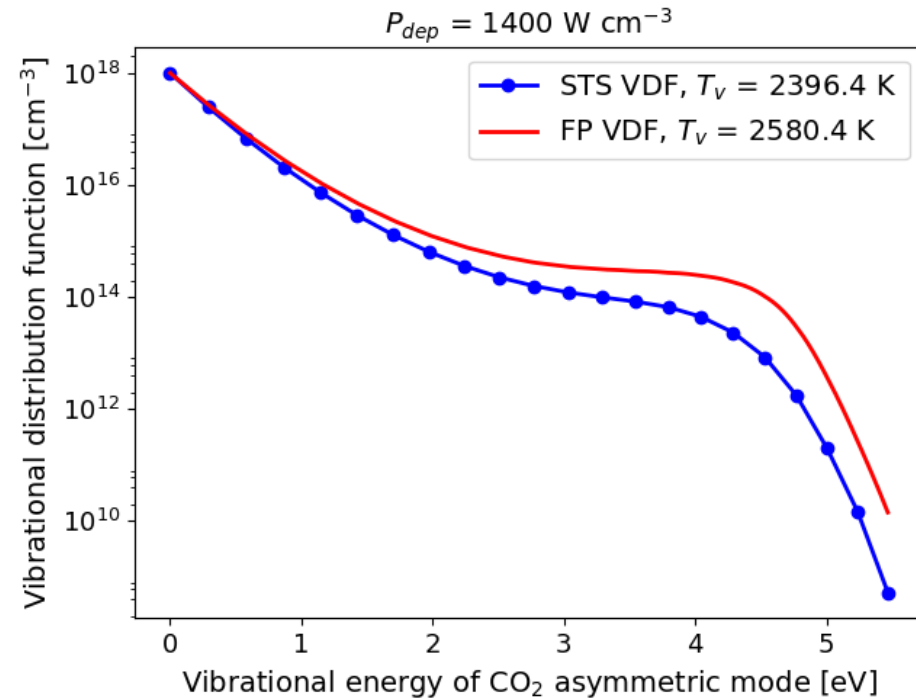
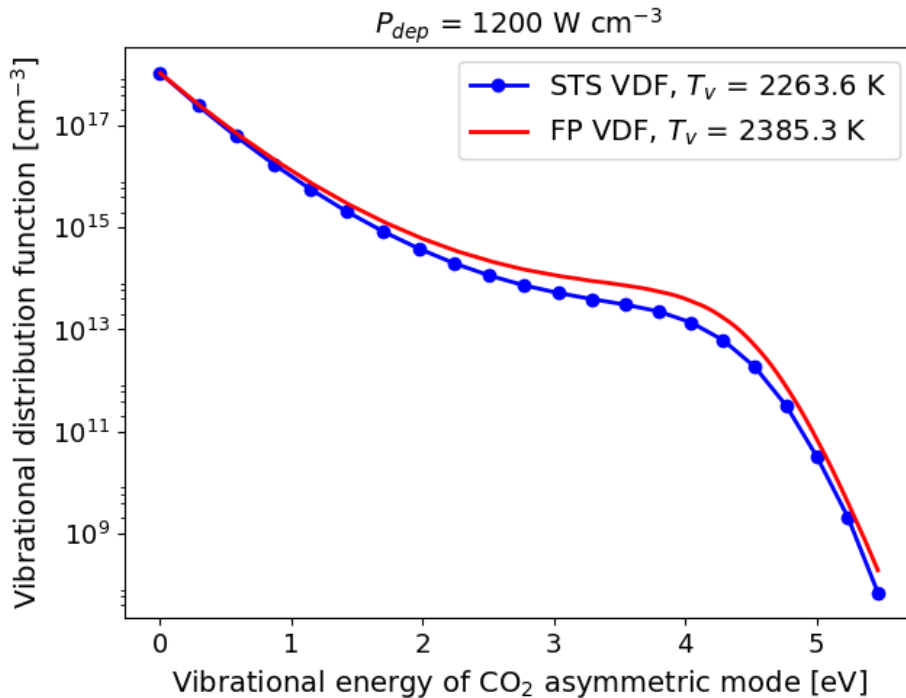
Benchmarking the FP approach (variation of P_{dep})



- T_V slightly higher with reduced STS – difference increases with P_{dep}
- Very good agreement on VDF



Benchmarking the FP approach (variation of P_{dep})



- T_v slightly higher with reduced STS – difference increases with P_{dep}
- Very good agreement on VDF for $T_v < 2500 \text{ K}$
- Correctness of FP approach is verified for $T_g = 300 \text{ K}$ and $T_v < 2500 \text{ K}$



Conclusions

- The correctness of the FP approach has been **verified** for use in **self-consistent** plasma models.
- The FP approach is much more **computationally efficient** for stationary solution than the full STS approach.
- The computational efficiency obtained by the FP approach is very promising for the **development of multidimensional models**.



Next steps

- Understand the influence of further chemical processes on VDF, and vice-versa, using the FP approach.
- Study of T_g dependence of FP coefficients and VDF.
- Use the self-consistent **FP model in conditions of experiments** with CO₂ plasma reactors.



Thank you for your attention

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