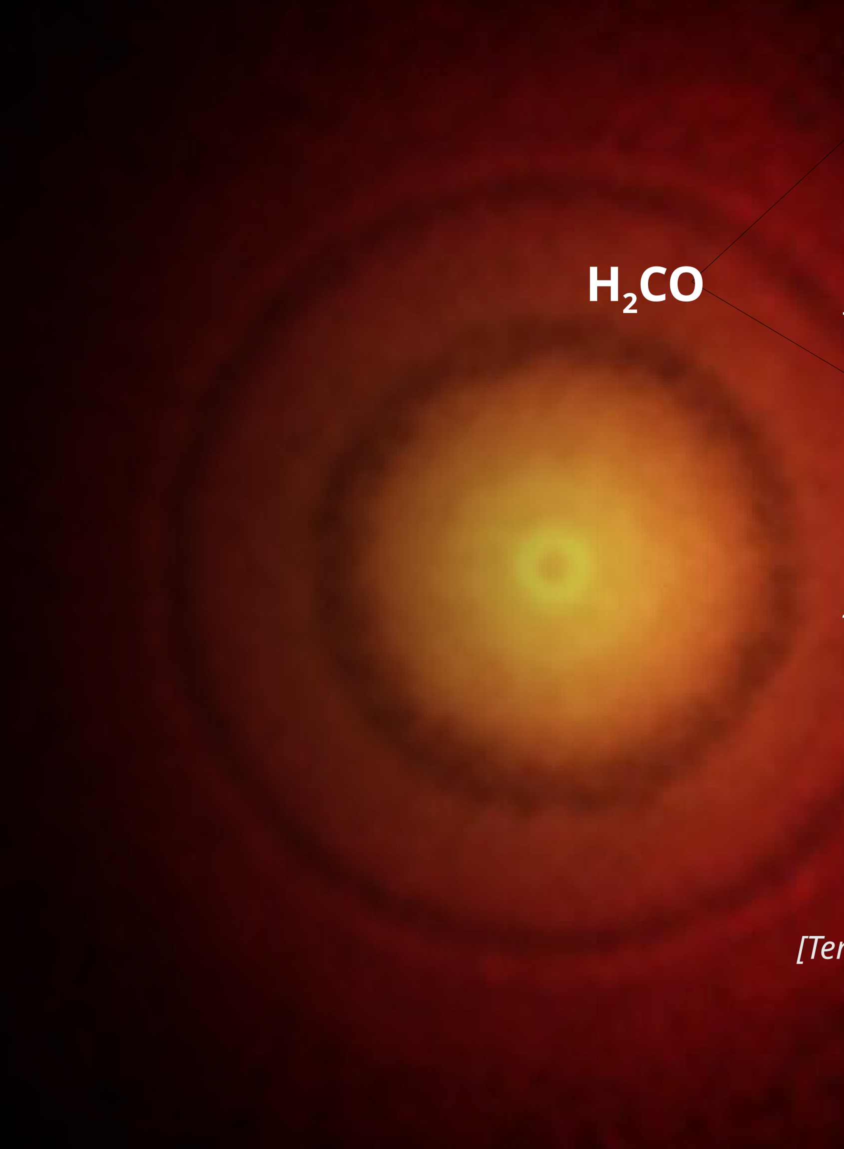
The ***ortho-para chemistry*** of H_2CO in ***protoplanetary disks***

M. Gaillard**, **A. Faure**, **P. Hily-Blant** and **R. Le Gal

Purpose: Exploiting **OPRs** as new physico-chemical **probes** of proto-planetary **disks**

TW Hya (ALMA 870 µm)



H_2CO

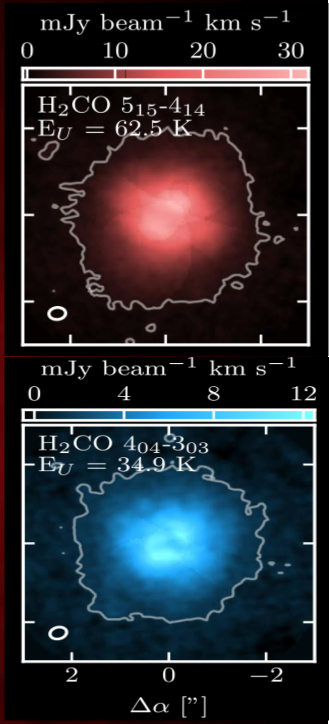
ortho

5_{12} - 4_{14}
351.768 GHz

para

4_{04} - 3_{03}
290.623 GHz

Spin isomers



[Terwisscha van Scheltinga et al. (2021)]

22th June 2026 – SF2A PCMI

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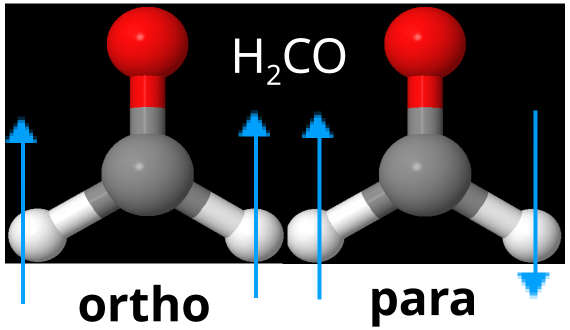
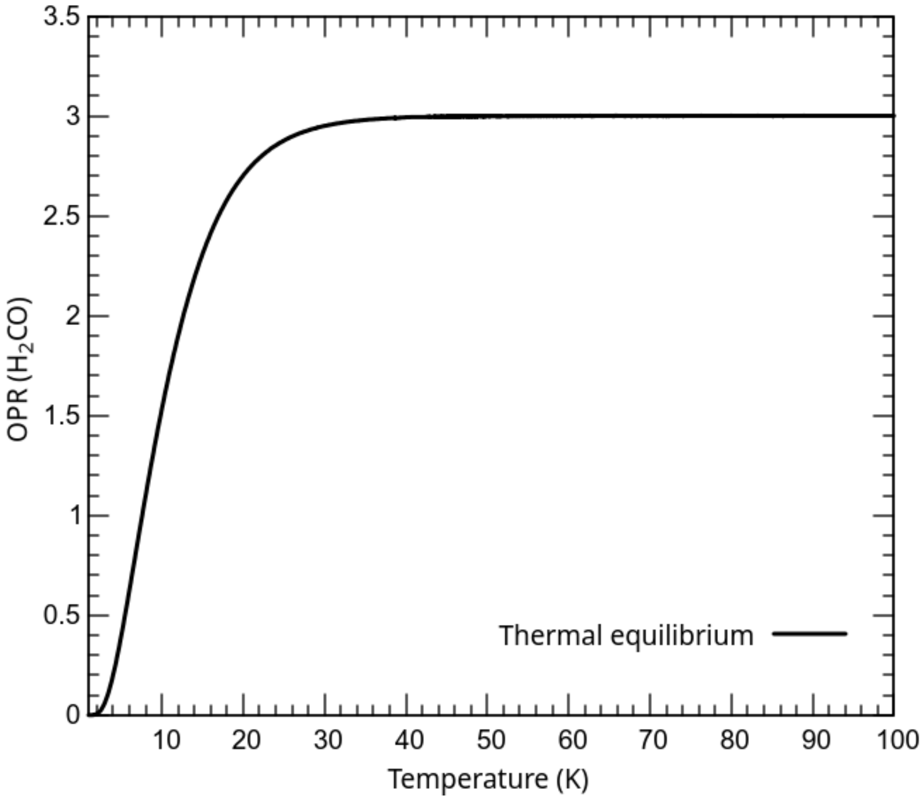
Introduction

Ortho-to-para ratios *(OPRs)*





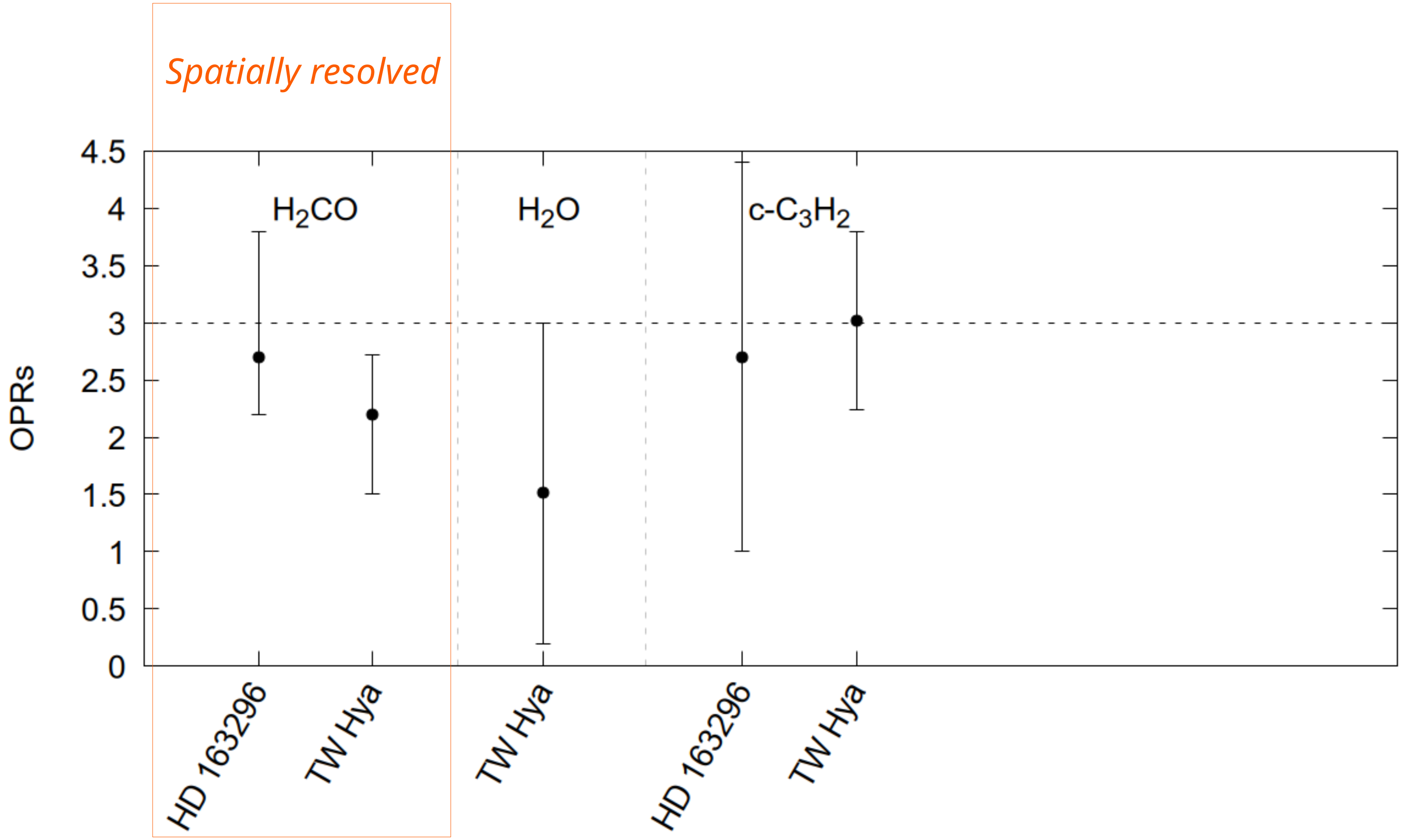
- **Comets**

- **Laboratory experiments :**
  - H_2O ices *[Hama et al. (2016)]*
  - H_2CO ices *[Yocum et al. (2023)]*

- **Modeling :**
  - NH_3 in molecular clouds *[Faure et al. (2013)]*
  - NH_3 deuterated isotopologues *[Hily-Blant et al. (2018); Harju et al. (2025)]*
  - H_2O in molecular clouds *[Faure et al. (2019)]*
  - *H_2CO in TW Hya* *[Gaillard et al. (2026), ACS Earth and Space Chemistry]*

Introduction

Ortho-to-para ratios *(OPRs)* in disks

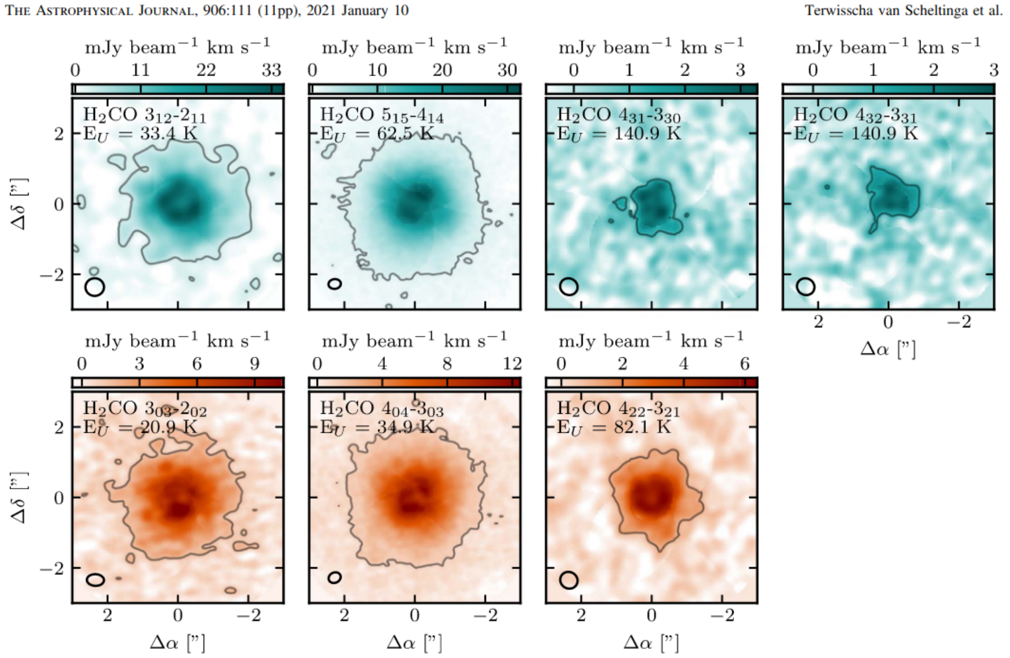


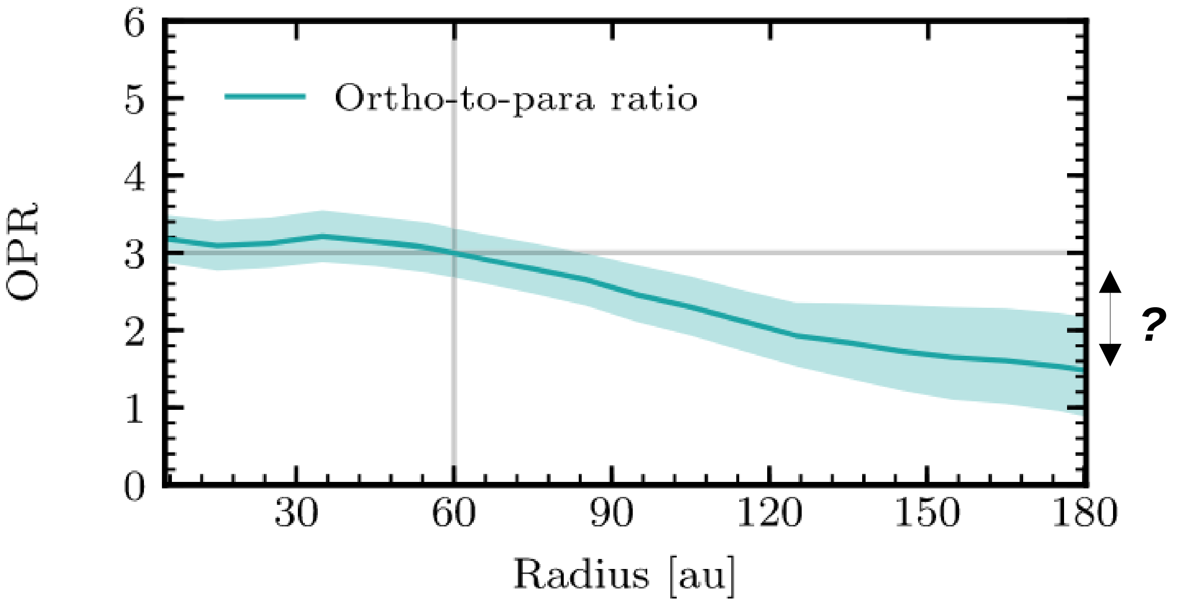
Observations

TW Hya

- Distance: ~ 50 pc
- Age: 7 – 10 Myrs *[Ruane et al. (2017)]*
- Stellar mass: 0.8 M⊙ *[Canta et al. (2021)]*
- Disk mass: 0.023 M⊙ *[Kama et al. (2016)]*

- OPR ≠ 3 above 60 au:
    - Gas-phase processes ?
    - Pebble drift below 60 au ?
    - Specificity of this disk ?



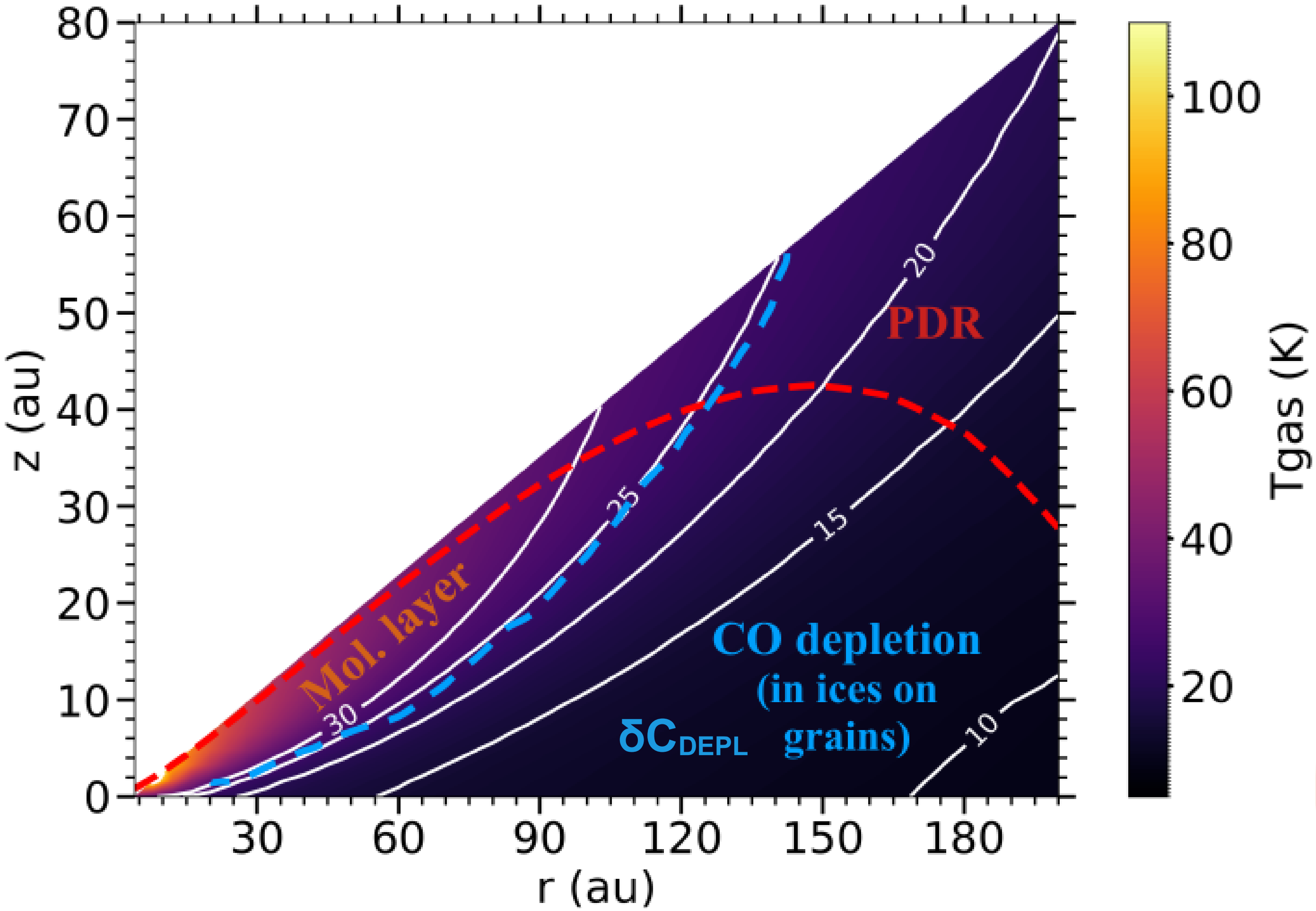


[Terwisscha van Scheltinga et al. (2021)]

Modeling

TW Hya

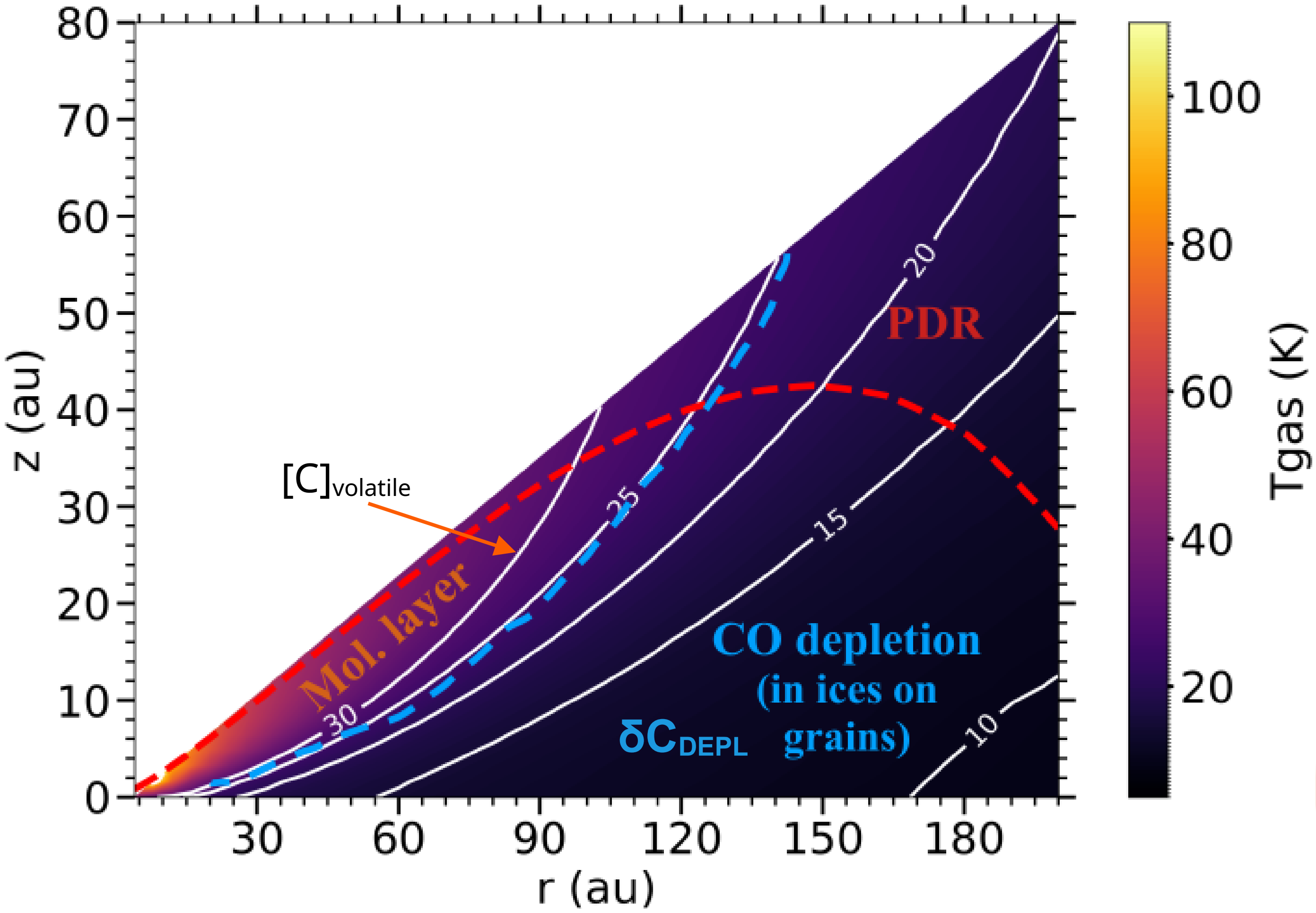
- **Assumptions/laws:**
  - Parametric modeling: Power laws
  - Steady-state abundances (10^6 - 10^7 yrs)



Modeling

TW Hya

- **Assumptions/laws:**
  - Parametric modeling: Power laws
  - Steady-state abundances (10^6 - 10^7 yrs)
  - Free parameters:
    - $[C/O]_{volatile} = 1$
    - $\zeta = 5 \times 10^{-19}\ s^{-1}$



Chemical Network

UGAN

Hily-Blant et al. (2018)

- **Nuclear spin isomers** of hydrides of C, N, O, S + **H_2CO**
- **Theory of Quack *(1977)***
    - Conservation of the total nuclear spin
    - Permutation symmetry
- Adapted to T < 100 K

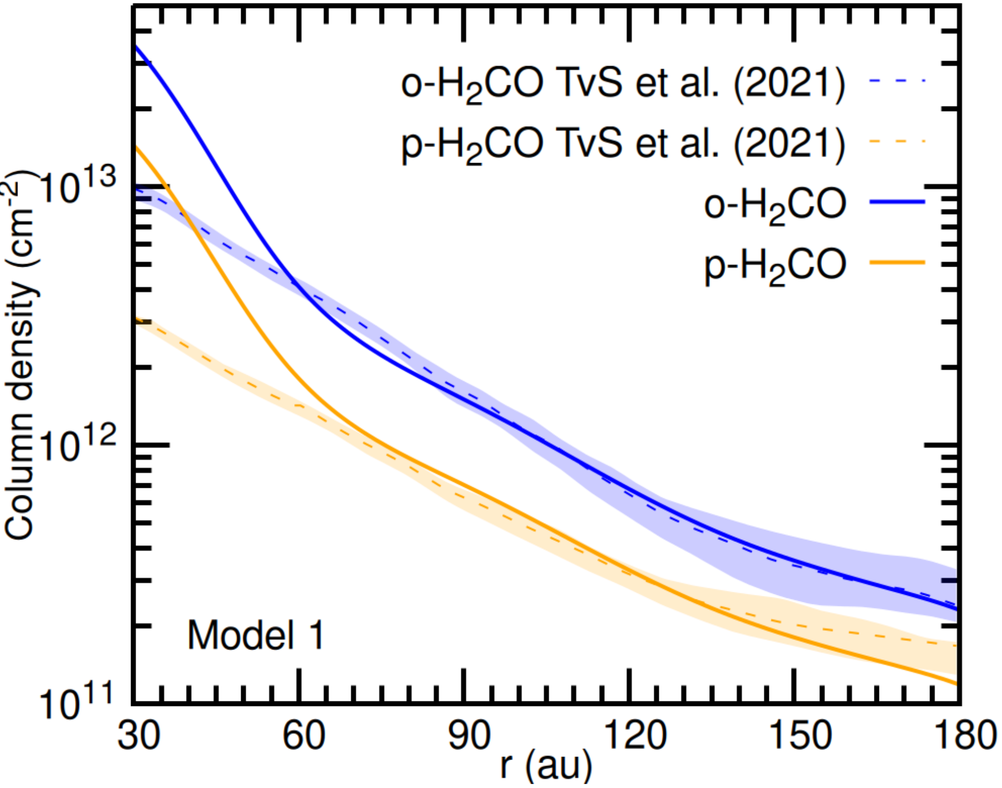
$$\text{o-CH}_3 + \text{O} \longrightarrow \text{o-H}_2\text{CO} \ + \text{H} \quad 1$$

$$\text{p-CH}_3 + \text{O} \longrightarrow \begin{cases} \text{o-H}_2\text{CO} \ + \text{H} & 1/2 \\ \text{p-H}_2\text{CO} \ + \text{H} & 1/2 \end{cases}$$

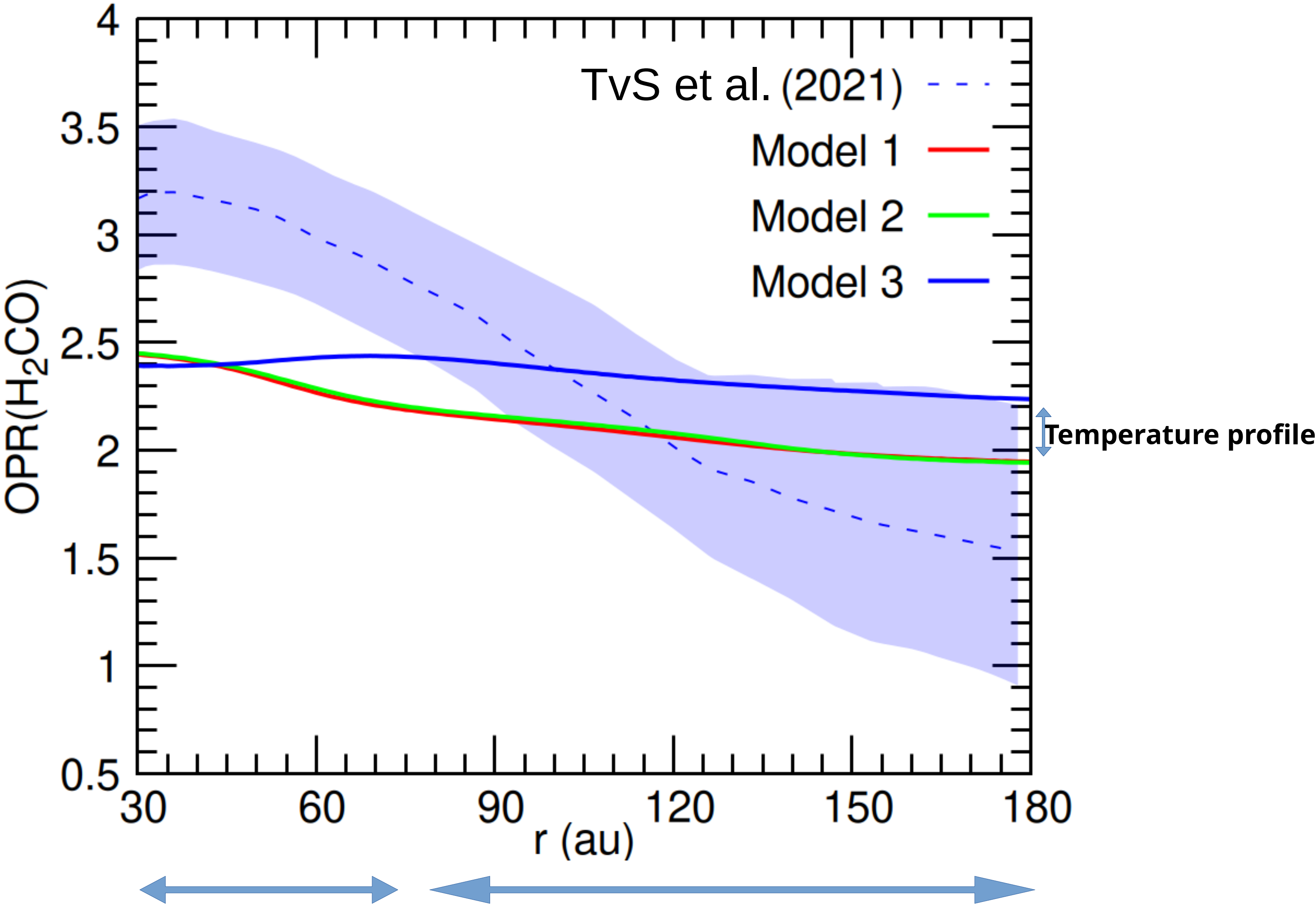
$$\begin{aligned} \text{H}_2\text{CO} + \text{C}_2\text{H} &\longrightarrow \text{C}_2\text{H}_2 + \text{HCO}, \\ &\longrightarrow \text{C}_2\text{H}_2 + \text{CO} + \text{H} \end{aligned}$$

Results

TW Hya



[M. Gaillard et al. : *ACS Earth and Space Chemistry* ***2026*** *10 (3)*, 687-696]



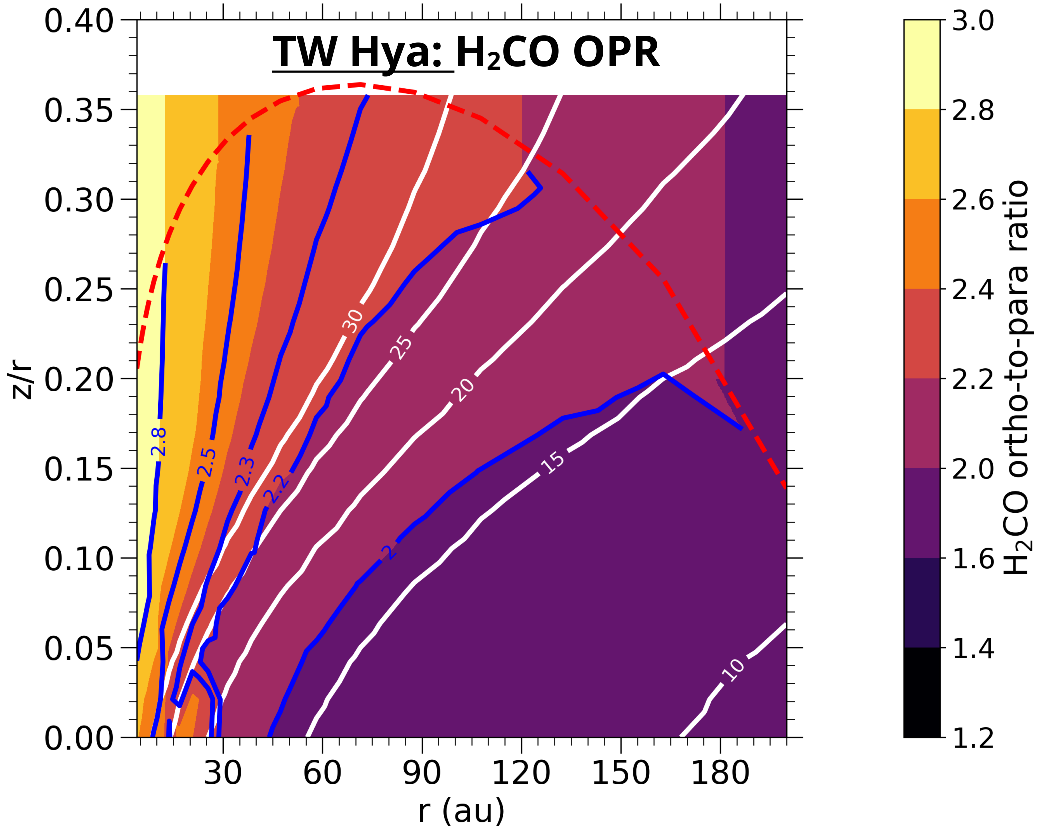
Temperature profile

Inner radius
(ice desorption?)

Outer radius

Conclusion

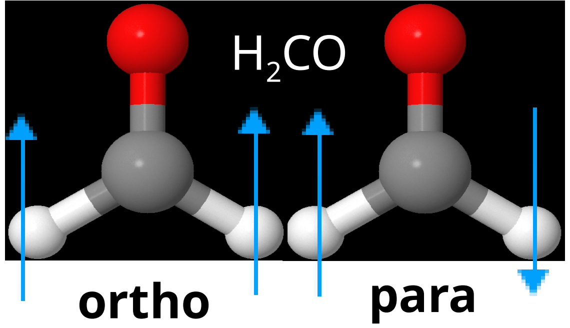
- **First model of H_2CO OPR chemistry in a disk**
- **H_2CO column densities :**
  - Sensitive to C/O and ζ
  - C_2H/H_2CO: a new C/O tracer
- **OPR :**
  - *A probe of kinetic temperature* →
  - Not sensitive to C/O and ζ
  - Inherited from H_2 via nuclear-spin selection rules
  - OPR ~ 3 below 60 au: pebble drift ?



- **Perspectives:**
  - Other disk environments (*HD 163296, DiskStrat ALMA LP PI: Romane Le Gal [see S16]*)
  - Explicit inclusion of adsorption and desorption : *next step*

Backup

H_2CO in UGAN



Formation :

- **Neutral-neutral**

$$\text{o-CH}_3 + \text{O} \longrightarrow \text{o-H}_2\text{CO} \; + \text{H} \quad 1$$

$$\text{p-CH}_3 + \text{O} \longrightarrow \begin{cases} \text{o-H}_2\text{CO} \; + \text{H} & 1/2 \\ \text{p-H}_2\text{CO} \; + \text{H} & 1/2 \end{cases}$$

55 % *[Xu et al. (2015)]*

Kinetic measurement above 300 K

- *Rate coefficient : 1.2×10^{-10} cm^{3}s^{-1}*

[Hack et al. (2005)]

H_2CO in UGAN

Destruction :

- **Ion-polar molecule**

$$H_2CO + HCO^+ \longrightarrow H_2COH^+ + CO$$

  - Capture theory *[Su & Chesnavich (1982)]*

    Rate coefficient ~ 8×10^{-9} cm^3s^{-1} (@ 30 K)

- **Neutral-radical**

$$\begin{aligned} H_2CO + CN &\longrightarrow HCN + HCO, \\ H_2CO + C_2H &\longrightarrow C_2H_2 + HCO, \\ &\longrightarrow C_2H_2 + CO + H \end{aligned}$$

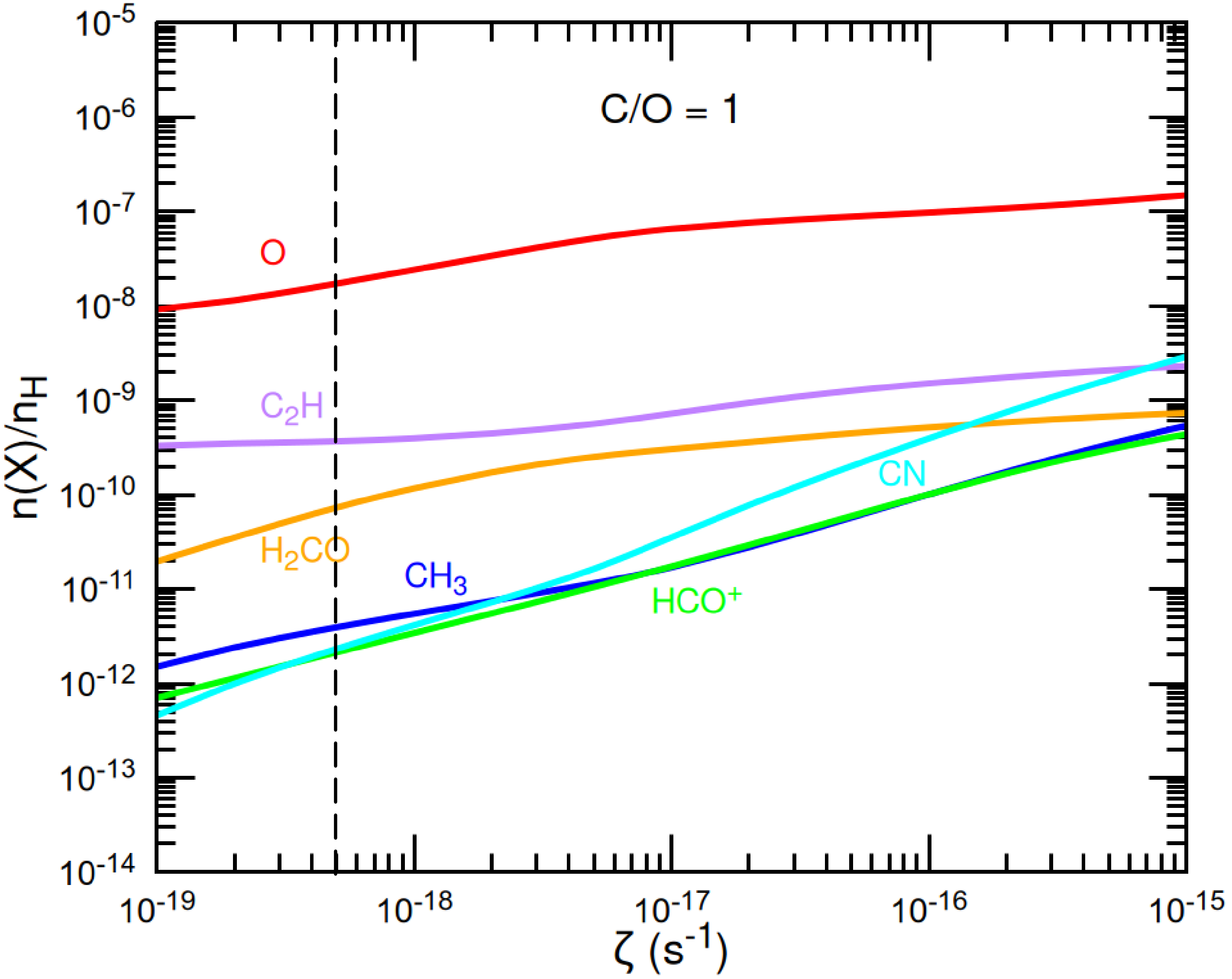
  - Measured down to 22 K for CN and 37 K for C_2H using the CRESU technique *[Douglas et al. (2023) & West et al. (2024) resp.]*

    Rate coefficient ~ 4×10^{-11} cm^3s^{-1} , ~ 1×10^{-10} cm^3s^{-1} (@ 22 K and 37 K *resp.*)

Impact of the CR ionization rate

- H_2CO abundance increases with ζ up to 10^{-16} s^{-1} as a result of CH_3 (precursor) and C_2H (destructor) evolution

$T_{gas} = 30$ K, $n_H = 10^8$ cm^{-3}



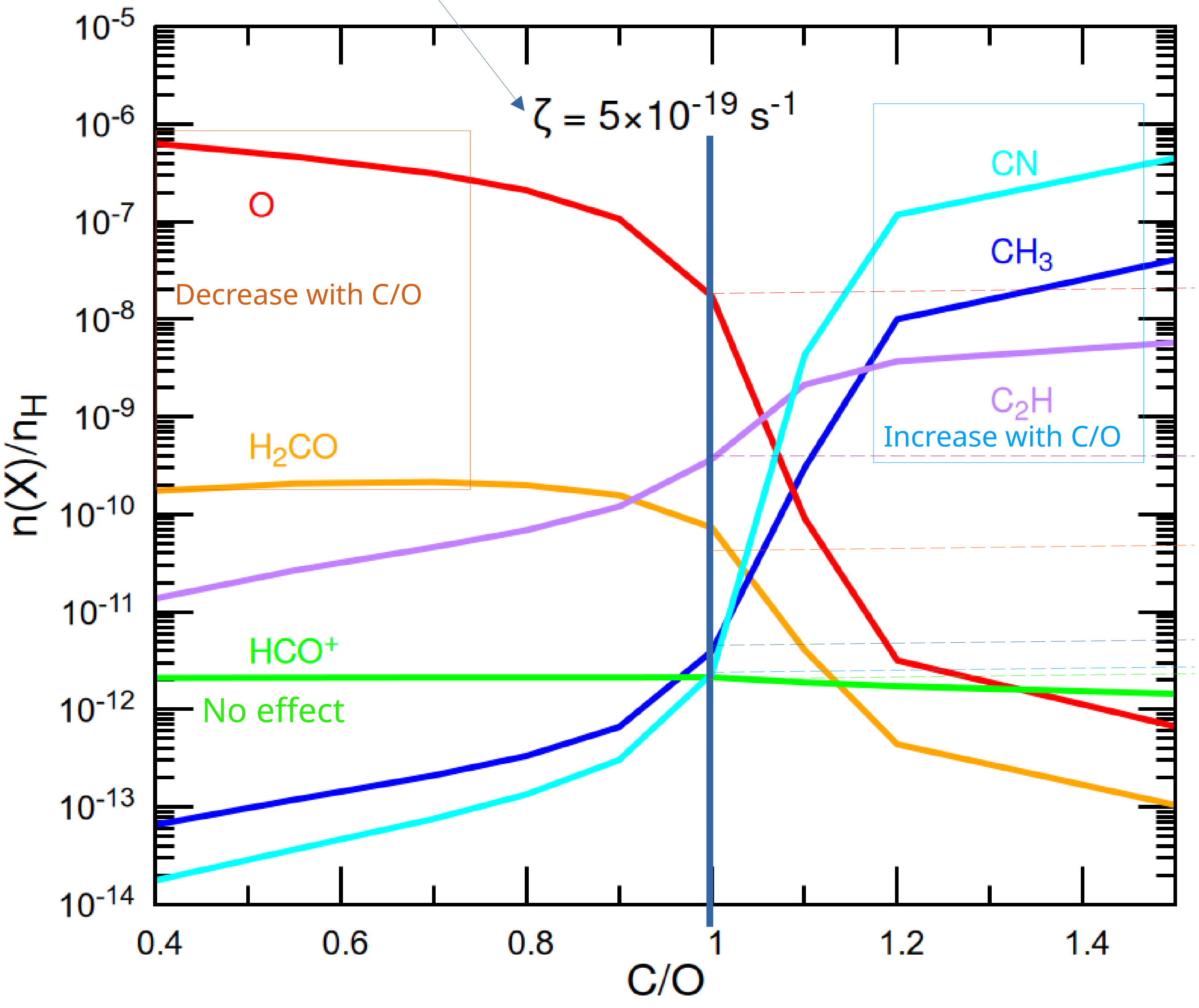
Impact to the C/O ratio

- **C/O < 1**: sufficient O remains available for formation of H_2CO → forms efficiently
- **C/O > 1**: most of O is locked in CO → strong decrease of H_2CO

CR ionization rate in our model of TW Hya

[Lee et al. (2024), Cleeves et al. (2018)]

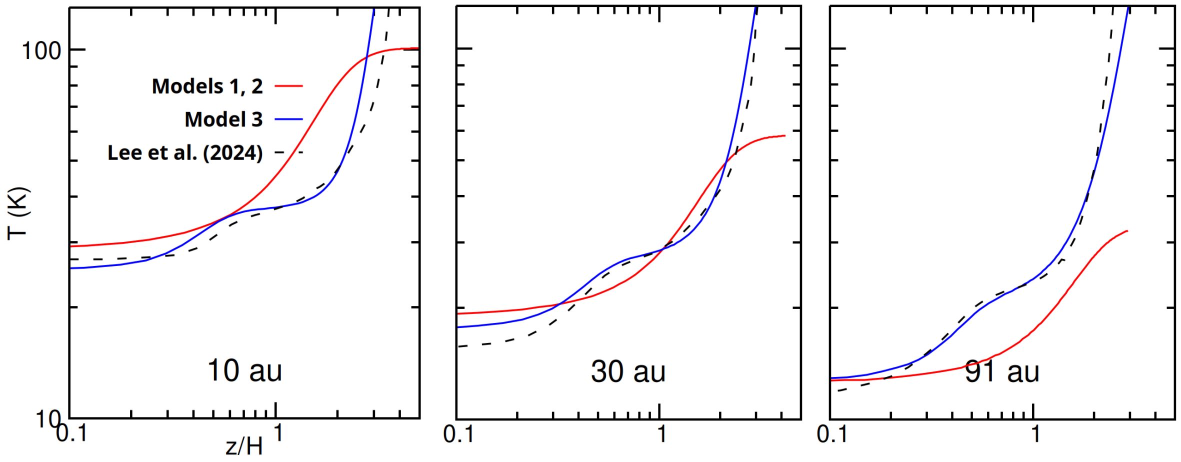
$T_{gas} = 30\ K,\ n_H = 10^8\ cm^{-3}$



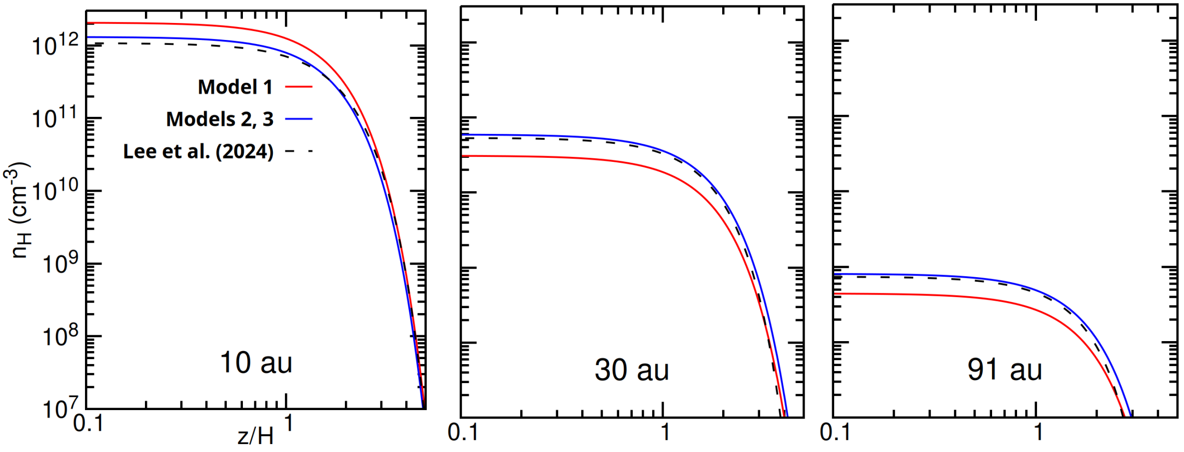
Physical structure of disk

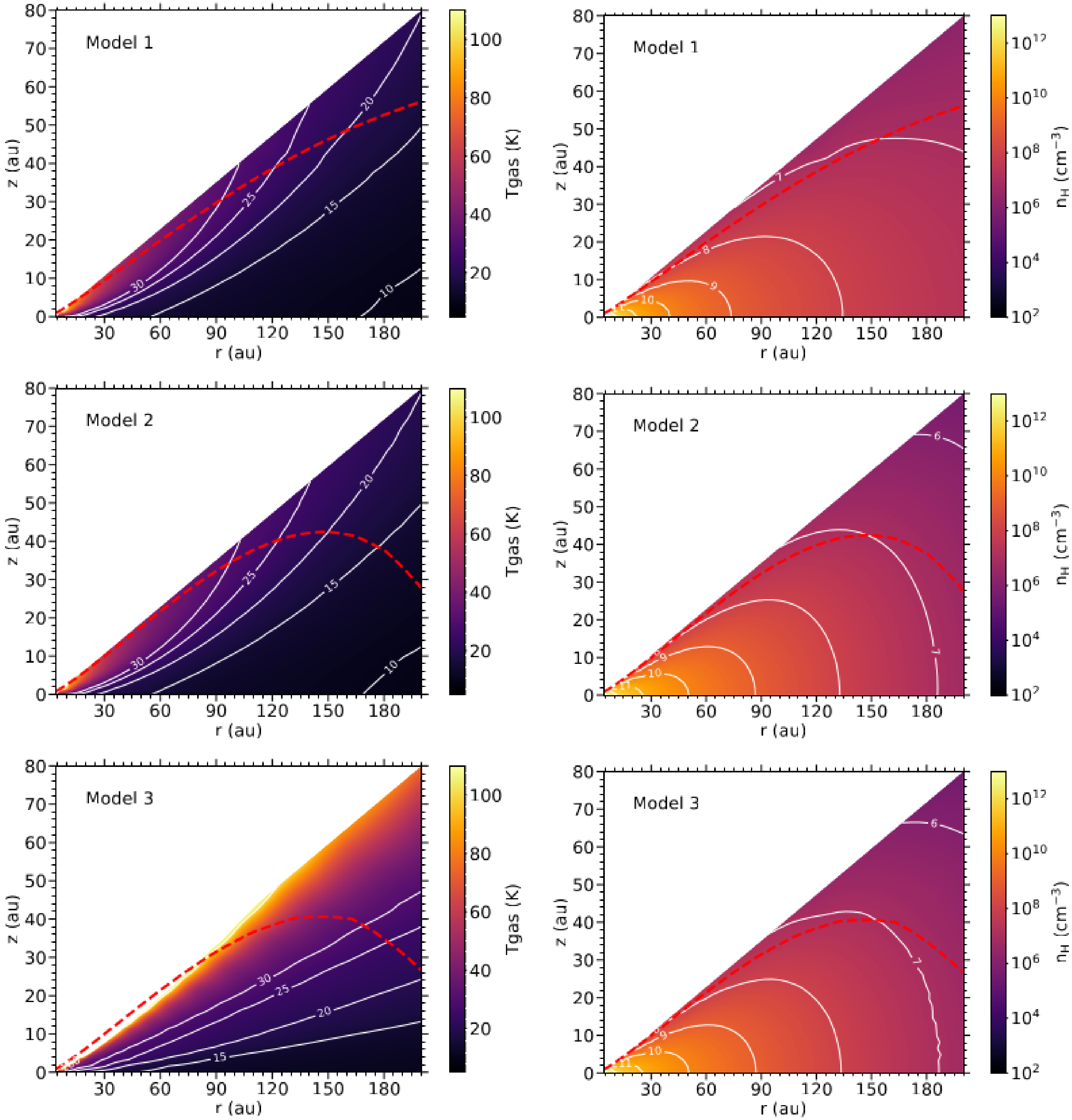
TW Hya

Vertical temperature profiles



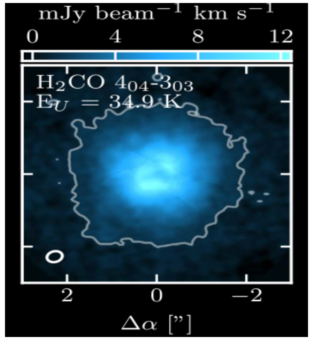
Vertical density profiles





Modeling

TW Hya



- **Initial gas-phase abundances :**
  - [C] = 2.75 × 10^{-6}
  - [O] = 2.75 × 10^{-6}
  - [N] = 4.2 × 10^{-5}
  - [S] = 8 × 10^{-8}

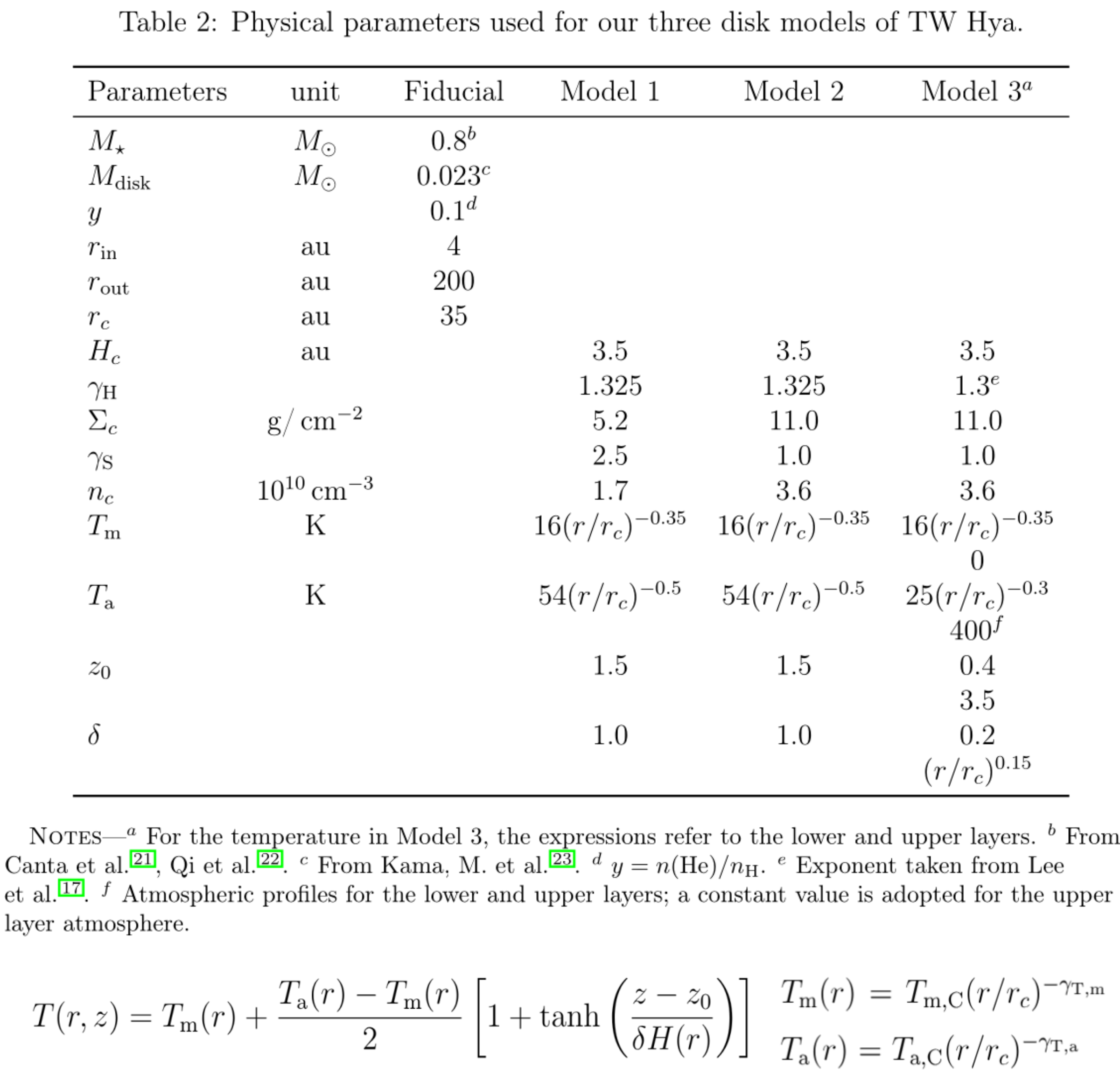


Table 2: Physical parameters used for our three disk models of TW Hya.

Parameters	unit	Fiducial	Model 1	Model 2	Model 3^a
$M_\star$	$M_\odot$	0.8^b			
$M_{\rm disk}$	$M_\odot$	0.023^c			
y		0.1^d			
$r_{\rm in}$	au	4			
$r_{\rm out}$	au	200			
r_c	au	35			
H_c	au		3.5	3.5	3.5
$\gamma_{\rm H}$			1.325	1.325	1.3^e
Σ_c	g/ cm^{-2}		5.2	11.0	11.0
$\gamma_{\rm S}$			2.5	1.0	1.0
n_c	10^{10} cm^{-3}		1.7	3.6	3.6
$T_{\rm m}$	K		$16(r/r_c)^{-0.35}$	$16(r/r_c)^{-0.35}$	$16(r/r_c)^{-0.35}$ 0
$T_{\rm a}$	K		$54(r/r_c)^{-0.5}$	$54(r/r_c)^{-0.5}$	$25(r/r_c)^{-0.3}$ 400^f
z_0			1.5	1.5	0.4 3.5
δ			1.0	1.0	0.2 $(r/r_c)^{0.15}$

NOTES—^{a} For the temperature in Model 3, the expressions refer to the lower and upper layers. ^{b} From Canta et al.[21], Qi et al.[22]. ^{c} From Kama, M. et al.[23]. ^{d} $y = n(\mathrm{He})/n_{\mathrm{H}}$. ^{e} Exponent taken from Lee et al.[17]. ^{f} Atmospheric profiles for the lower and upper layers; a constant value is adopted for the upper layer atmosphere.

$$T(r,z) = T_{\rm m}(r) + \frac{T_{\rm a}(r) - T_{\rm m}(r)}{2}\left[1 + \tanh\left(\frac{z - z_0}{\delta H(r)}\right)\right] \qquad \begin{aligned} T_{\rm m}(r) &= T_{\rm m,C}(r/r_c)^{-\gamma_{\rm T,m}} \\ T_{\rm a}(r) &= T_{\rm a,C}(r/r_c)^{-\gamma_{\rm T,a}} \end{aligned}$$

[Gaillard et al. (2026), ACS Earth and Space Chemistry]

H_2CO in UGAN

Rates :

- **Modified Arrhenius law**

$$k(T) = \alpha\,(T/300)^{\beta}\exp(-\gamma/T)$$

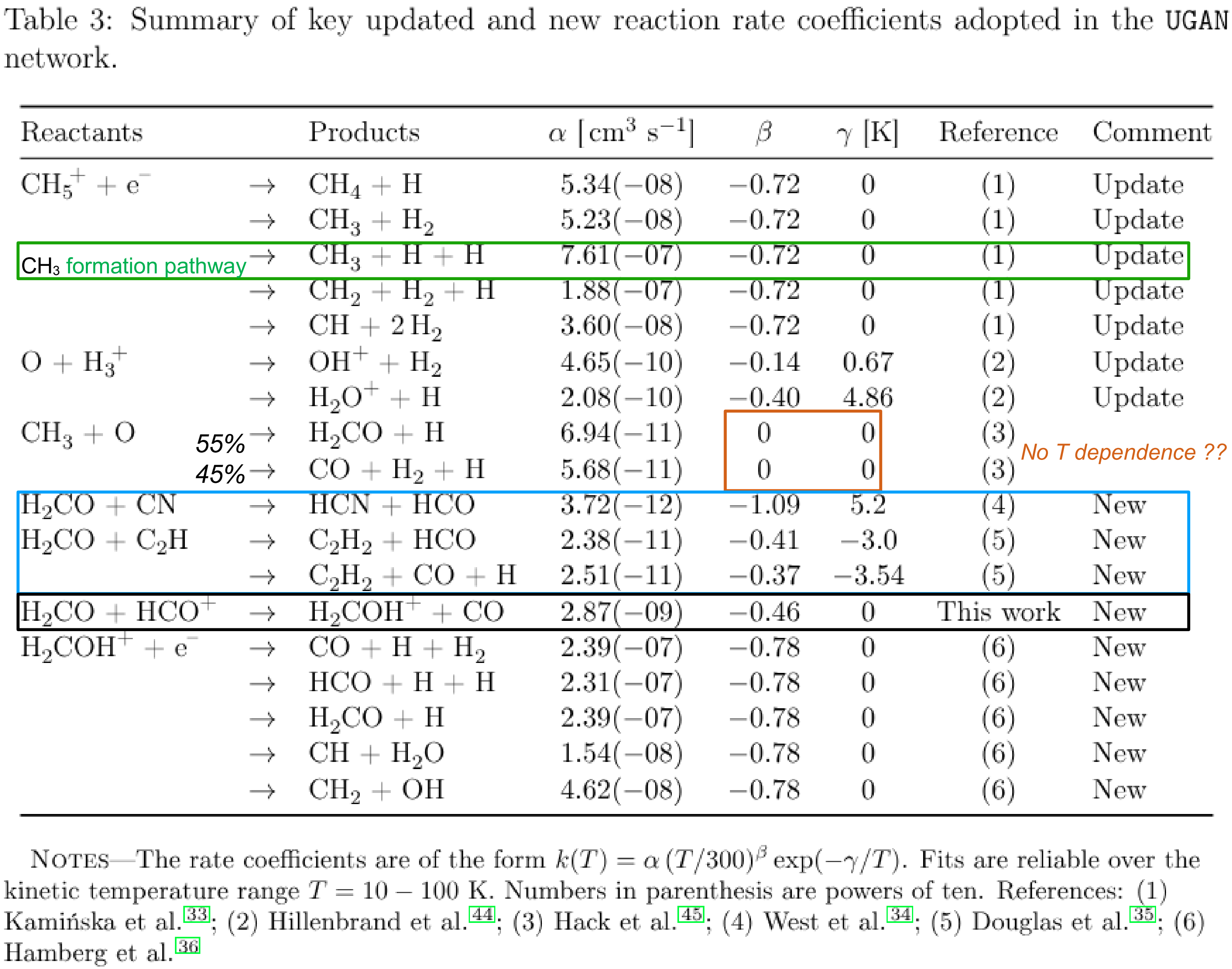


Table 3: Summary of key updated and new reaction rate coefficients adopted in the `UGAN` network.

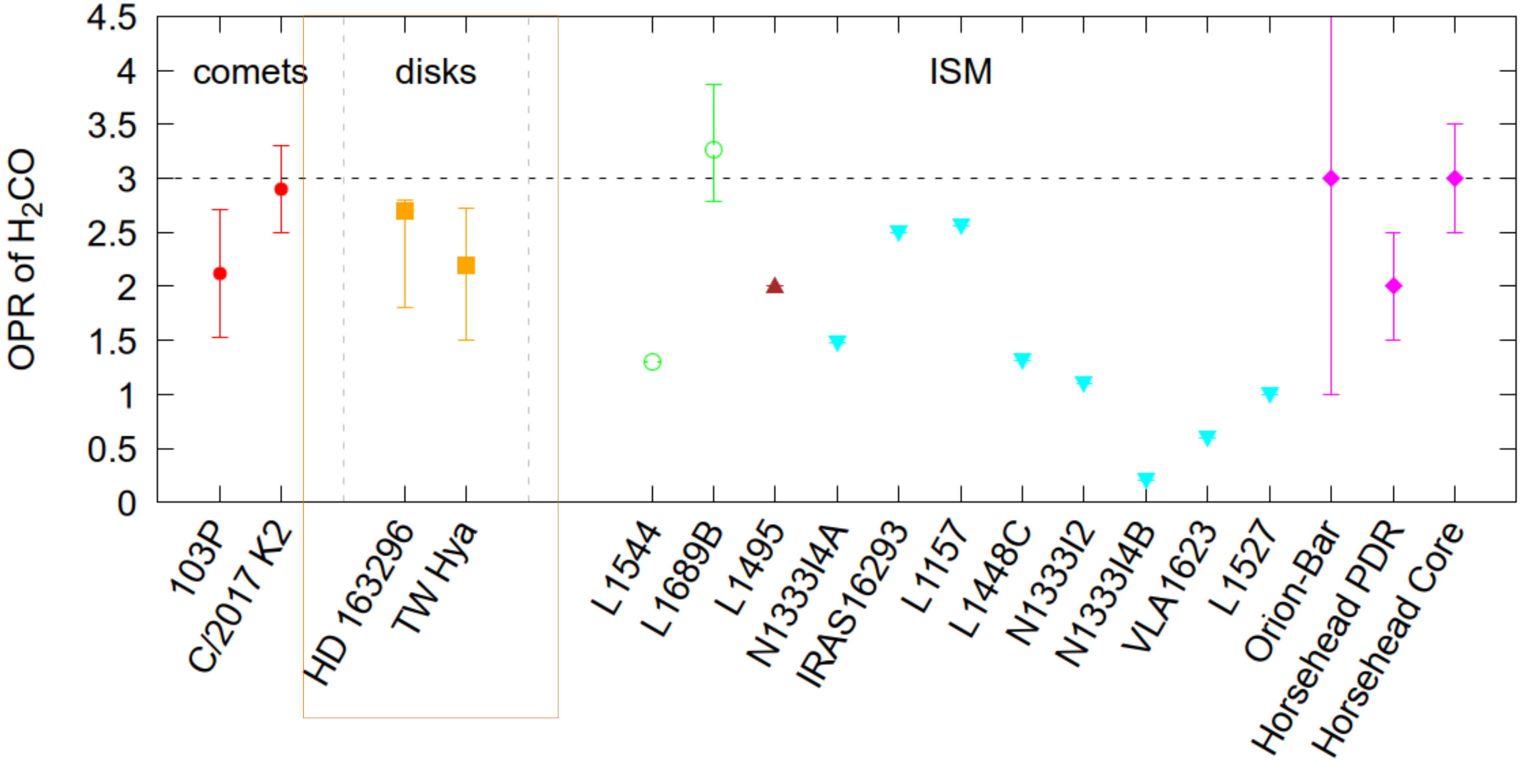
Reactants		Products	α [$cm^3\ s^{-1}$]	β	γ [K]	Reference	Comment
$CH_5^+ + e^-$	→	$CH_4 + H$	5.34(−08)	−0.72	0	(1)	Update
	→	$CH_3 + H_2$	5.23(−08)	−0.72	0	(1)	Update
CH_3 formation pathway	→	$CH_3 + H + H$	7.61(−07)	−0.72	0	(1)	Update
	→	$CH_2 + H_2 + H$	1.88(−07)	−0.72	0	(1)	Update
	→	$CH + 2\,H_2$	3.60(−08)	−0.72	0	(1)	Update
$O + H_3^+$	→	$OH^+ + H_2$	4.65(−10)	−0.14	0.67	(2)	Update
	→	$H_2O^+ + H$	2.08(−10)	−0.40	4.86	(2)	Update
$CH_3 + O$	55% →	$H_2CO + H$	6.94(−11)	0	0	(3)	No T dependence ??
	45% →	$CO + H_2 + H$	5.68(−11)	0	0	(3)	
$H_2CO + CN$	→	$HCN + HCO$	3.72(−12)	−1.09	5.2	(4)	New
$H_2CO + C_2H$	→	$C_2H_2 + HCO$	2.38(−11)	−0.41	−3.0	(5)	New
	→	$C_2H_2 + CO + H$	2.51(−11)	−0.37	−3.54	(5)	New
$H_2CO + HCO^+$	→	$H_2COH^+ + CO$	2.87(−09)	−0.46	0	This work	New
$H_2COH^+ + e^-$	→	$CO + H + H_2$	2.39(−07)	−0.78	0	(6)	New
	→	$HCO + H + H$	2.31(−07)	−0.78	0	(6)	New
	→	$H_2CO + H$	2.39(−07)	−0.78	0	(6)	New
	→	$CH + H_2O$	1.54(−08)	−0.78	0	(6)	New
	→	$CH_2 + OH$	4.62(−08)	−0.78	0	(6)	New

NOTES—The rate coefficients are of the form $k(T) = \alpha\,(T/300)^{\beta}\exp(-\gamma/T)$. Fits are reliable over the kinetic temperature range $T = 10 - 100$ K. Numbers in parenthesis are powers of ten. References: (1) Kamińska et al.[33]; (2) Hillenbrand et al.[44]; (3) Hack et al.[45]; (4) West et al.[34]; (5) Douglas et al.[35]; (6) Hamberg et al.[36]

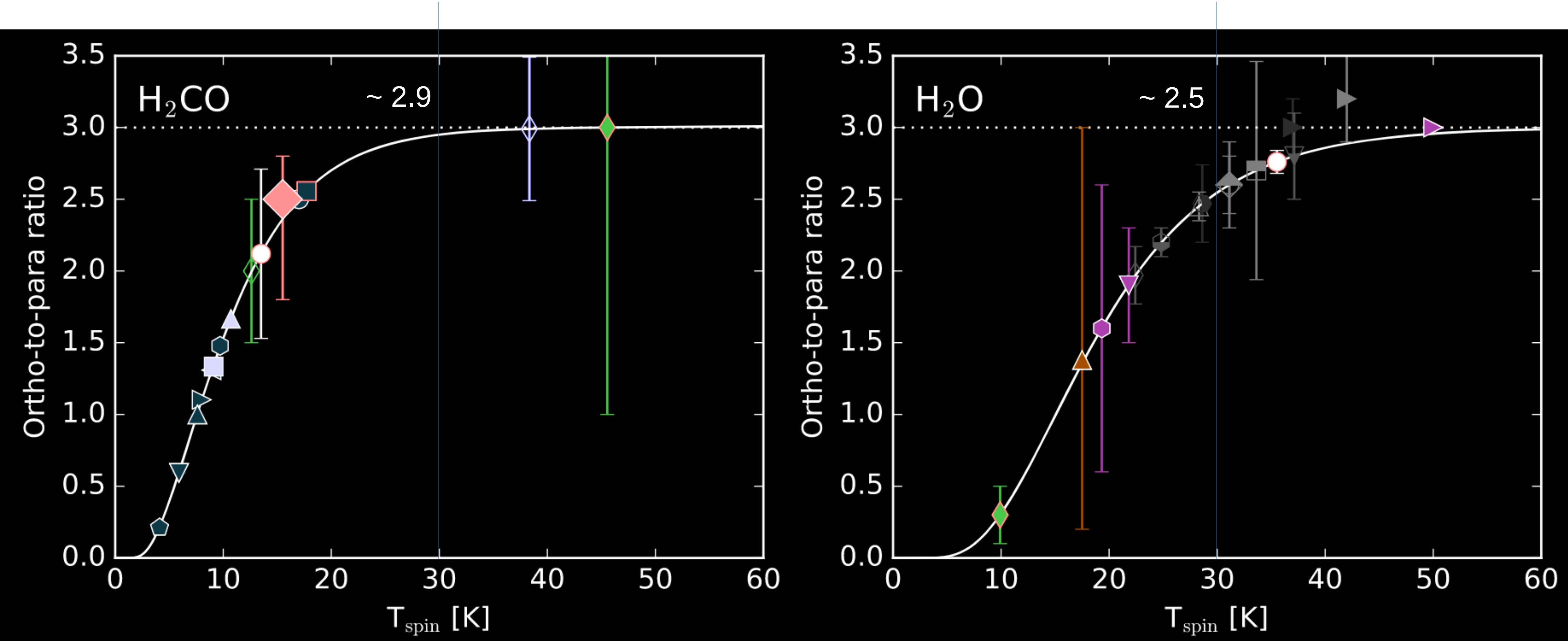
Introduction

Context:

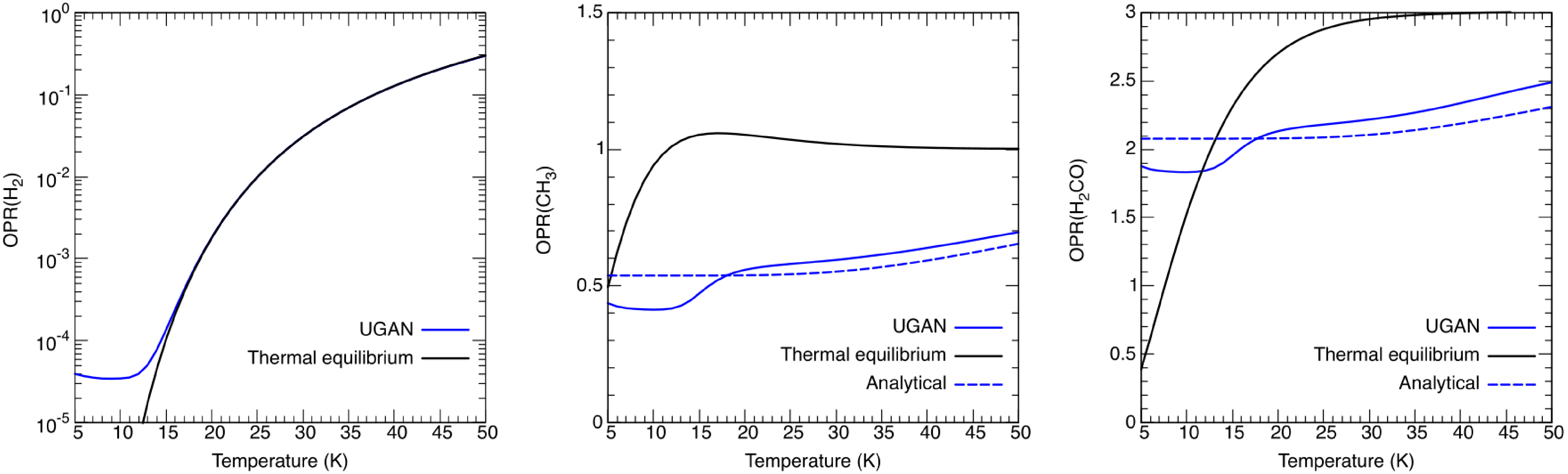
Ortho-to-para ratios *(OPRs)* of H_2CO



OPR H_2CO VS H_2O



[Guzman et al. (2018)]



H_2CO OPR is governed by H_2 OPR

Analytical OPRs departs from the UGAN values :

$$\mathrm{OPR}(\mathrm{H_2CO}) = 1 + 2\mathrm{OPR}(\mathrm{CH_3}) = \frac{27 + 31\mathrm{OPR}(\mathrm{H_2})}{13 + 9\mathrm{OPR}(\mathrm{H_2})}$$

temperature dependence of the OPR of CH_3^+ reactions in UGAN :

In *para*-rich H_2 gas :

$\mathrm{OPR}(\mathrm{CH_3}){=}7/13 \sim 0.54$ and $\mathrm{OPR}(\mathrm{H_2CO}){=}27/13 \sim 2.1.$

$H_2COH^+ + e^- \rightarrow H_2CO$