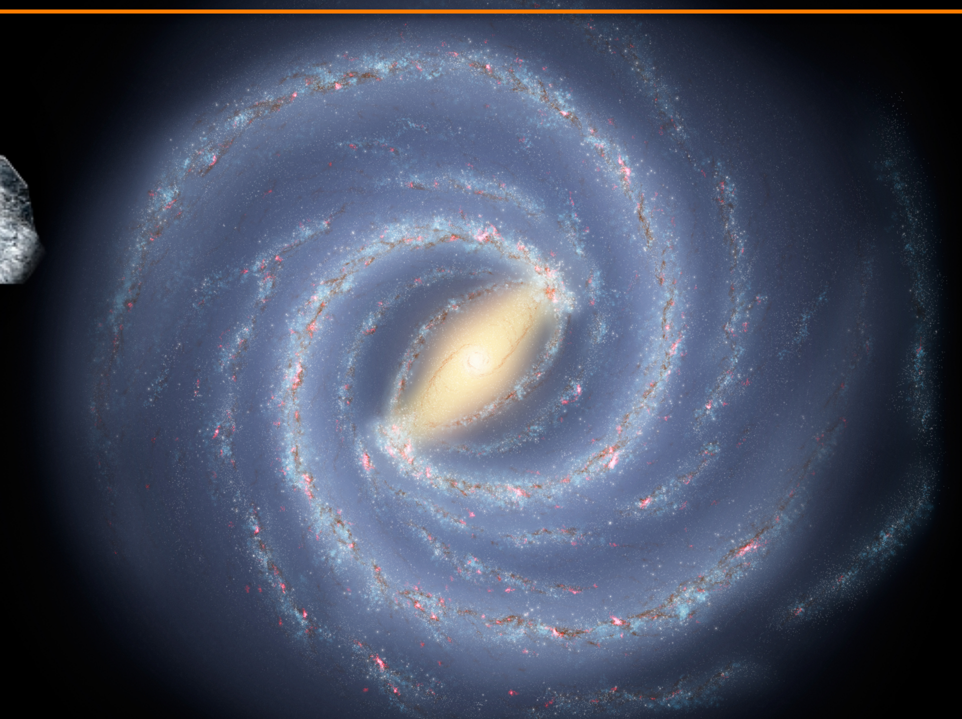
The key role of nuclear-spin astrochemistry in the ISM



Romane Le Gal

Research Associate (UVa)
in Eric Herbst's group

Collaborators: Changjian Xie, Hua Guo (UNM), Dahbia Talbi (LUPM), Carina Persson and Sebastien Muller (Chalmers, Sweden)

Outline

- **Interest and observations**
  - ortho-to-para ratios (OPRs) in the interstellar medium (ISM)
  - The NH_2 and H_2Cl^+ cases
- **Astrochemical modeling**
  - Building chemical network
  - Results: comparison with observations

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- Multi-hydrogenated species can present different spin configurations

  => distinguishable forms: e.g. para and ortho for di- and tri-hydrogenated species (depending on their total nuclear spin I)

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Multi-hydrogenated species OPRs: potential probes of the H_2 chemistry, starting point of all chemistry in molecular clouds

OPR measurements in the ISM

- <u>70's:</u> OPR of H_2 in diffuse gas (Spitzer+1973)
- <u>80's:</u> H_2CO in dense molecular clouds (Kahane+1984), H_2CS (Gardner+1985)
- <u>21st century</u>: C_3H_2 (Takakuwa+2001), CH_2 (Polehampton+2005), H_3^+ (Crabtree+2011), H_2O (Lis+2013, Flagey+2013), NH_3 (Persson+2012), NH_2 (Persson+2016), H_2S (Crokett+2014), H_2O^+ (Schilke+2010), H_2Cl^+ (Lis+2010), CH_2CN (Vastel+2015)

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- Spontaneous radiative o-p interconversions are extremely slow, e.g. ≈ 10^{13} yr for H_2 >> to the age of the Universe!

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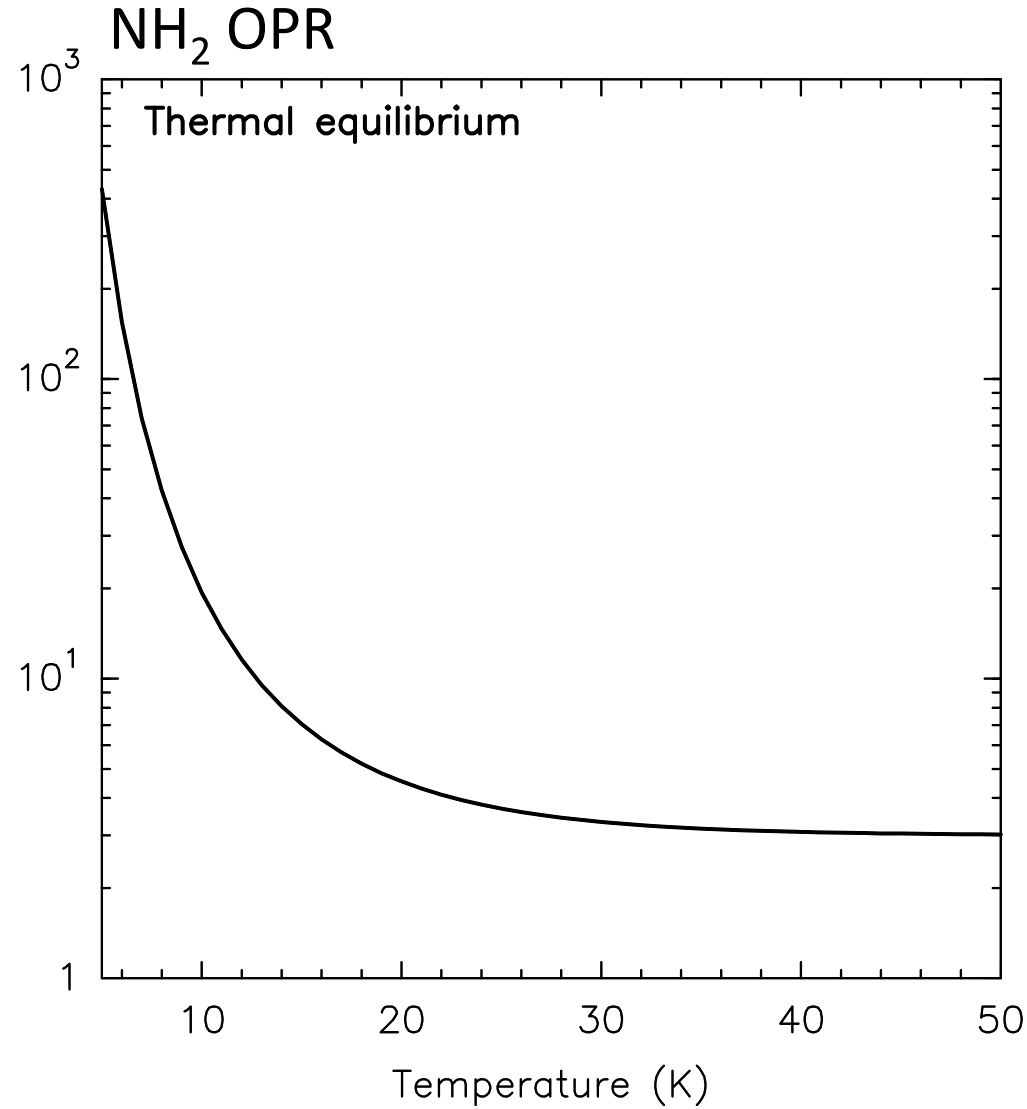
Further theoretical studies needed to explain the OPR discrepancies from their thermal equilibrium

NH_2 OPR thermal equilibrium with T

$$\mathrm{OPR}(T_{\mathrm{kin}}) = \frac{3\sum_J^{ortho} g_J \exp(-E_{J_{K_a,K_c}}/k_B T)}{\sum_J^{para} g_J \exp(-E_{J_{K_a,K_c}}/k_B T)}$$



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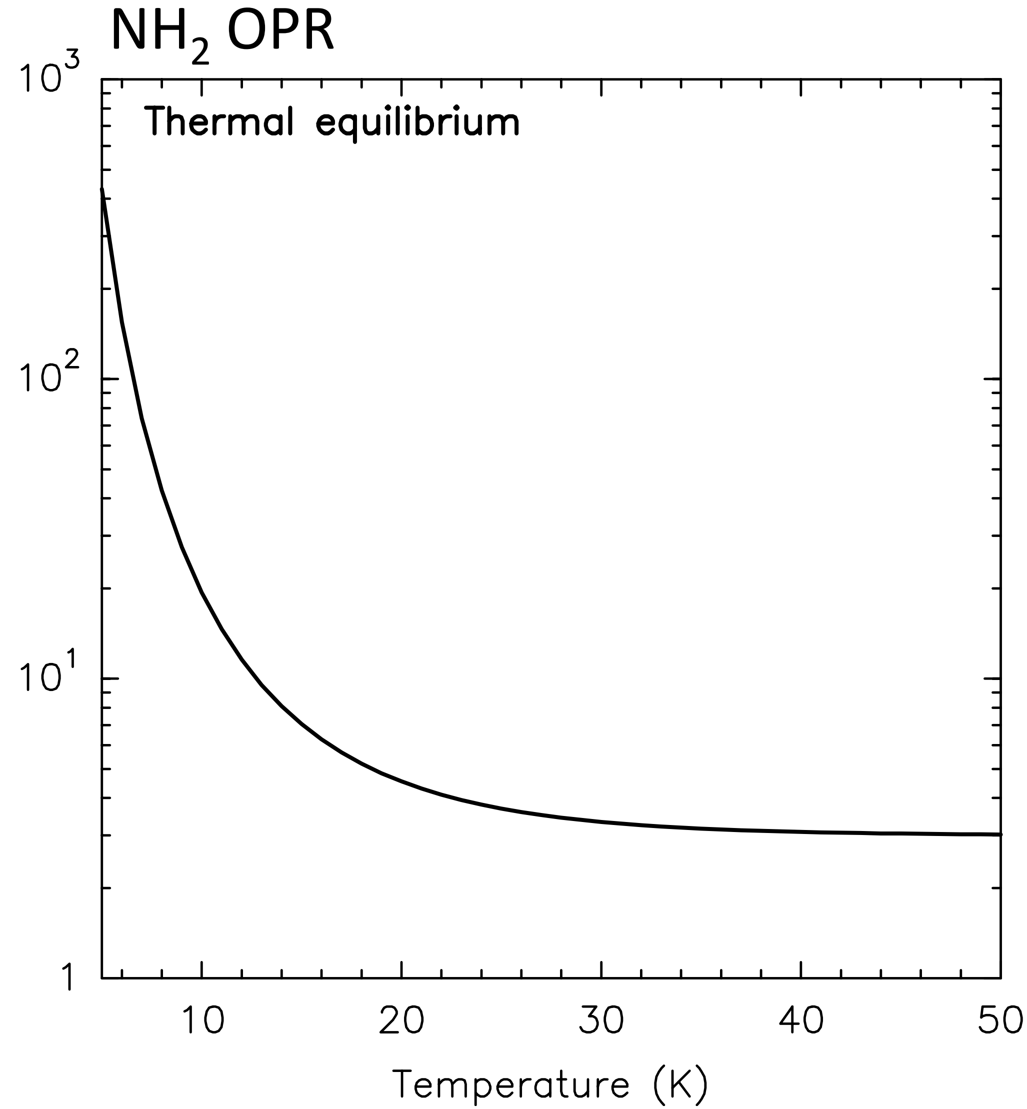
$$\mathrm{OPR}(T_{\mathrm{low}}) \approx \exp\left(\frac{-\Delta E}{T_{\mathrm{kin}}}\right) = \exp\left(\frac{30.4}{T_{\mathrm{kin}}}\right)$$



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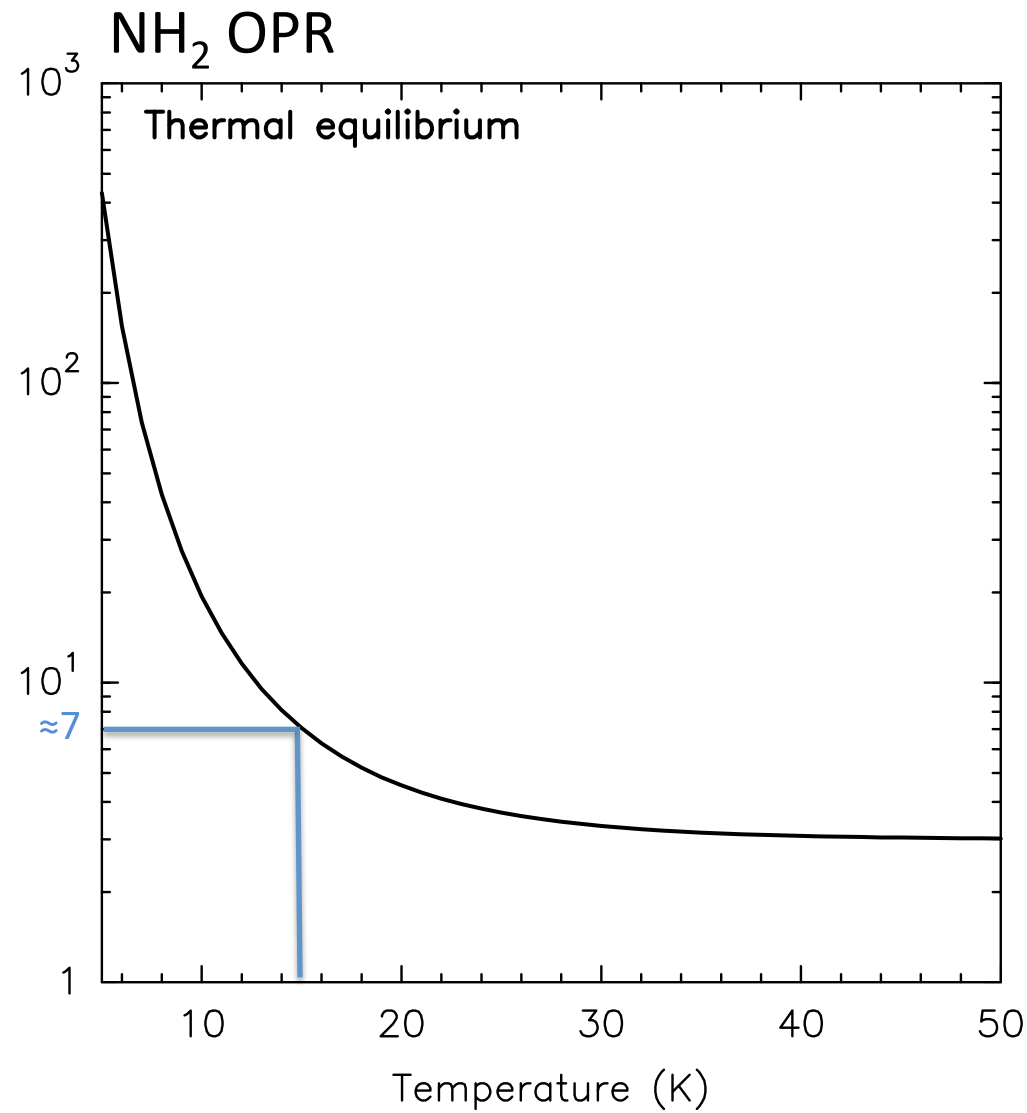

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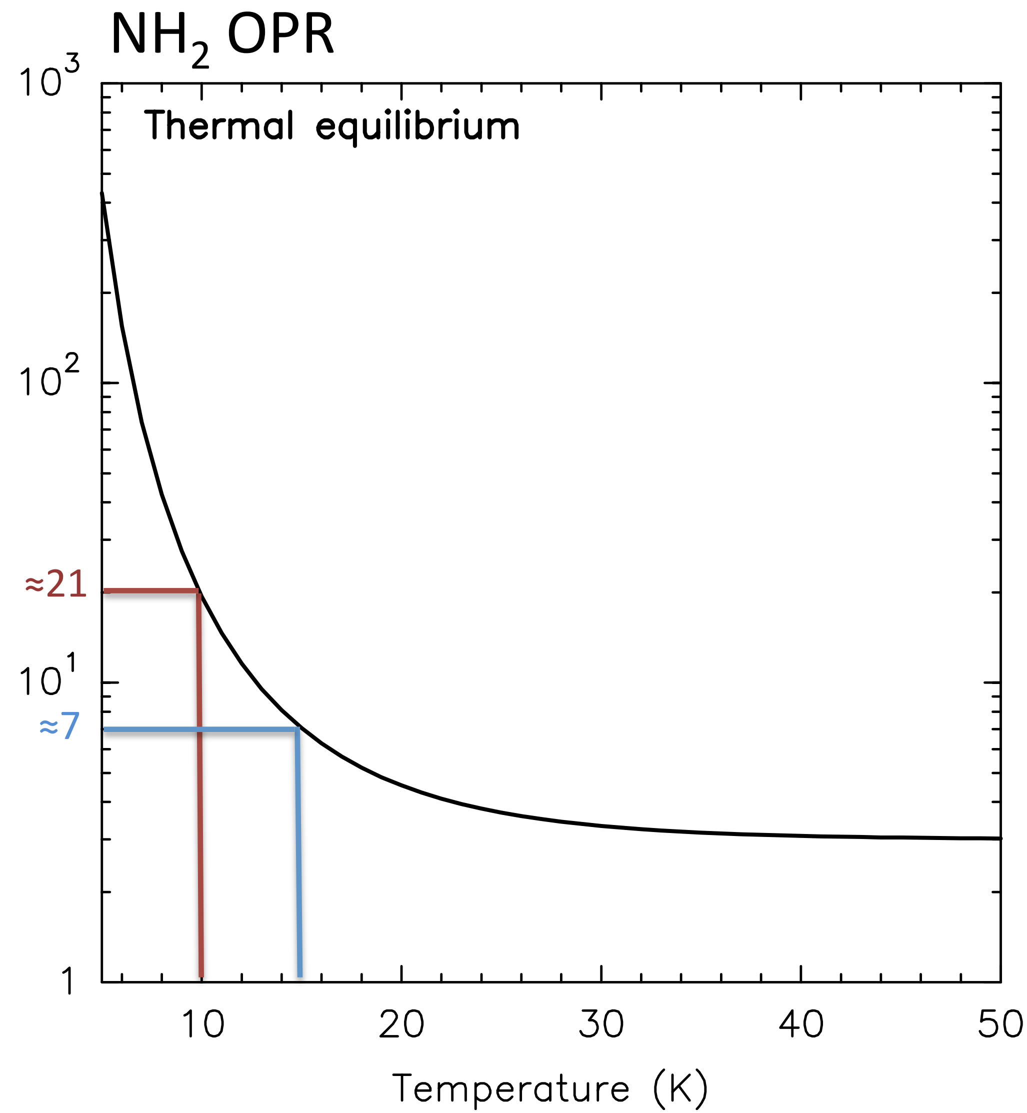
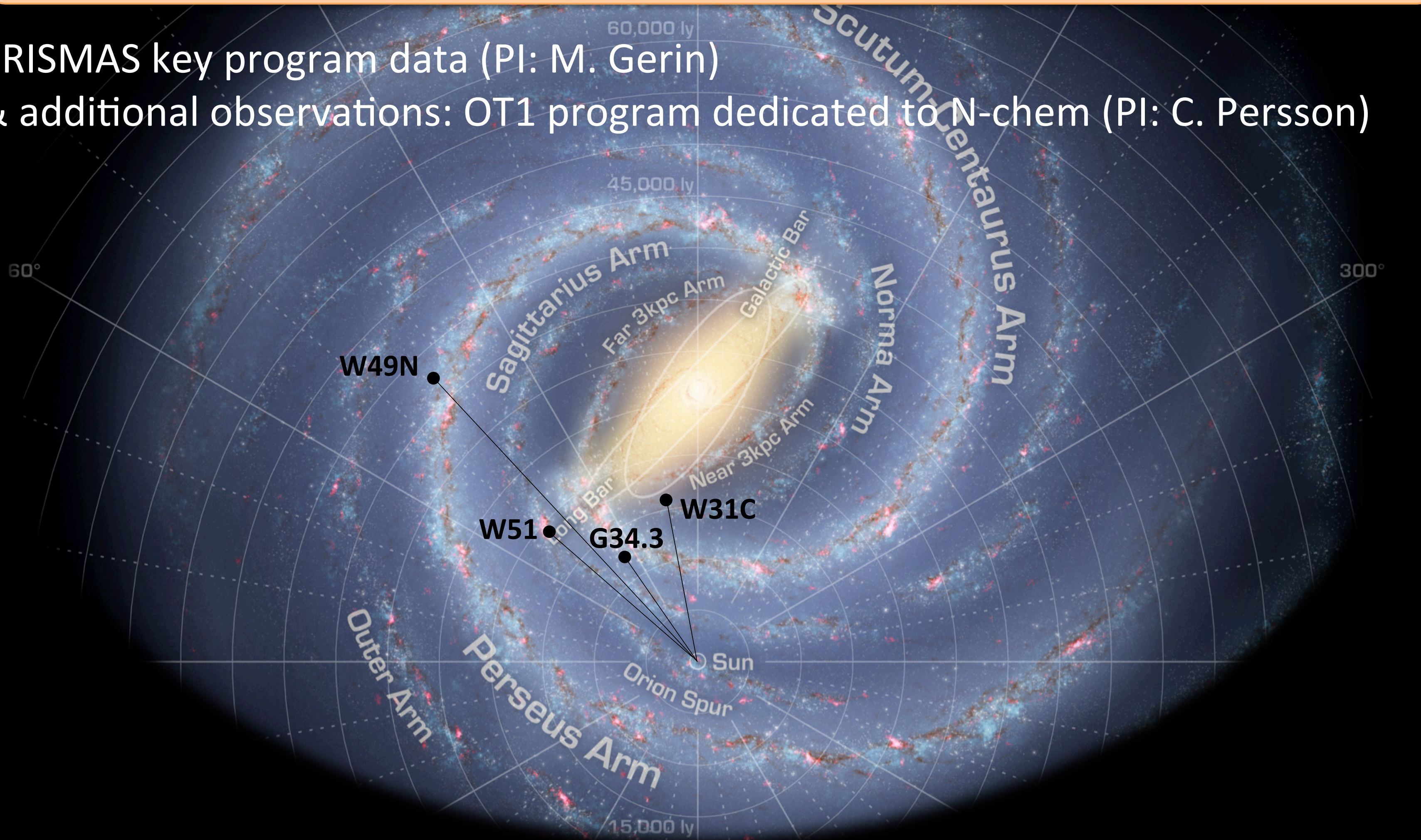
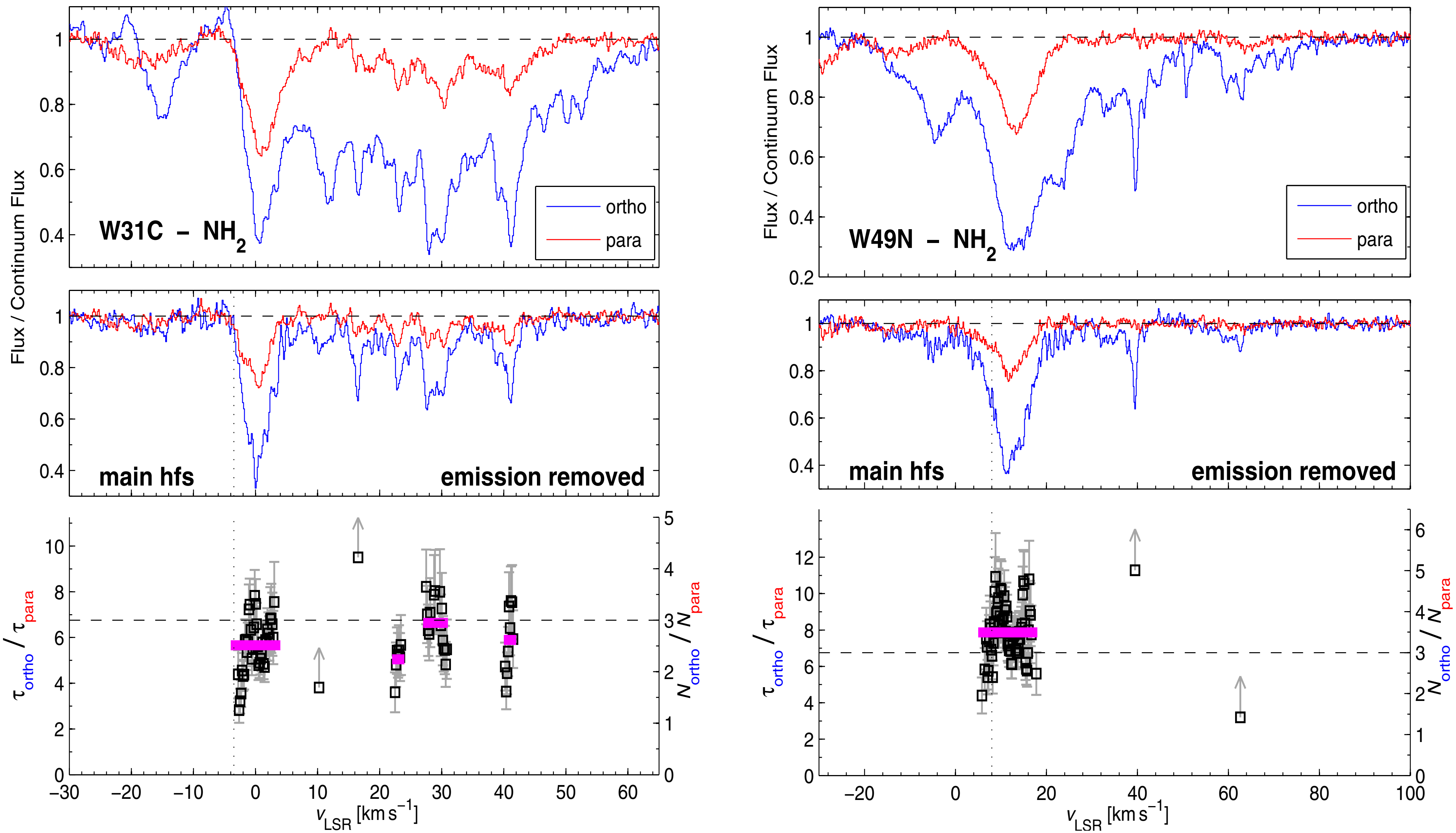


Interstellar NH_2 OPR toward star-forming regions

PRISMAS key program data (PI: M. Gerin)
& additional observations: OT1 program dedicated to N-chem (PI: C. Persson)

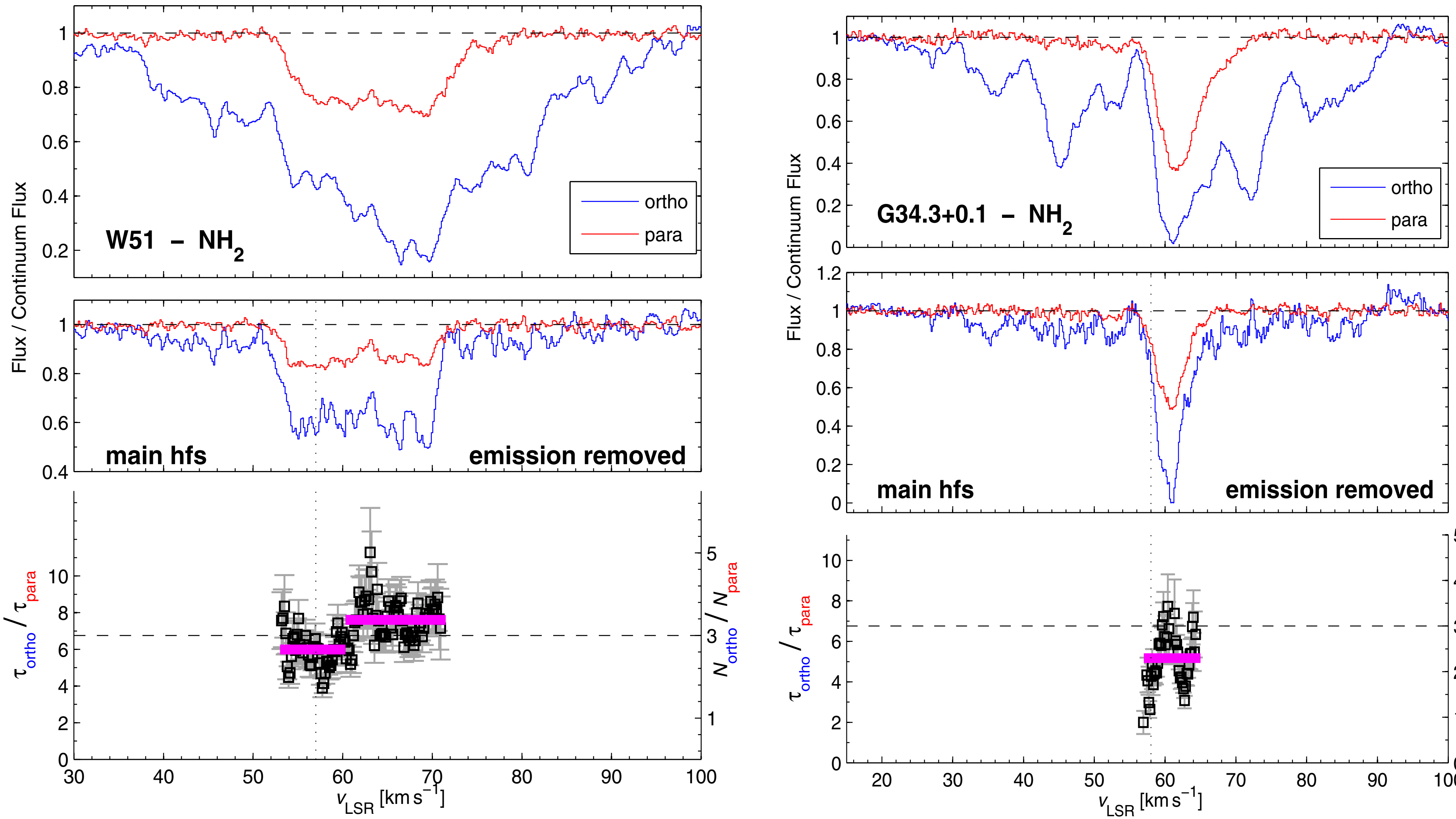


NH_2 OPR toward W31C &W49N



*Persson, Olofsson, **Le Gal** et al., A&A. (2016)*

NH_2 OPR toward W51 & G34.3



*Persson, Olofsson, **Le Gal** et al., A&A. (2016)*

Interstellar H_2Cl^+ OPR toward galactic sources

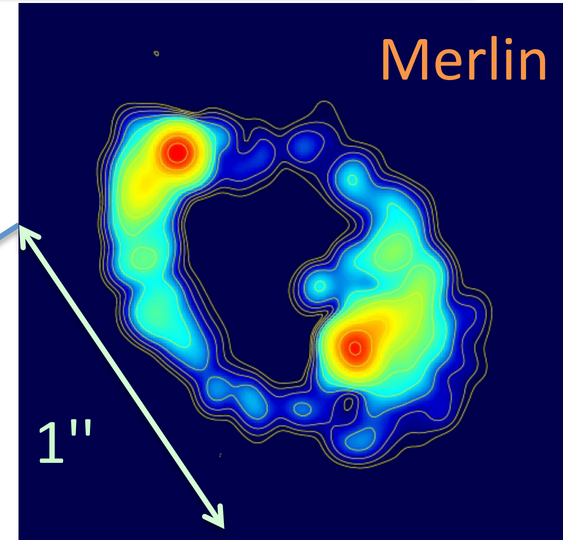
- <u>Lis et al. 2010</u>: ortho-H_2Cl^+ (1_{10}- 1_{01}) and para-H_2Cl^+ (1_{11}- 0_{00}) with Herschel/HIFI in absorption toward NGC 6334I => **OPR≈3**

- <u>Neufeld et al. 2012</u>: para-H_2Cl^+ (1_{11}- 0_{00}) with Herschel/HIFI:
  in absorption toward Sgr A, W31C, Orion MC, AFGL 2591
  in emission in OMC 1 (Orion Bar and Orion South)
- <u>Gerin et al. 2013</u>: ortho-H_2Cl^+ (1_{10}- 1_{01}) with 30 meter and CSO toward W31C and W49N

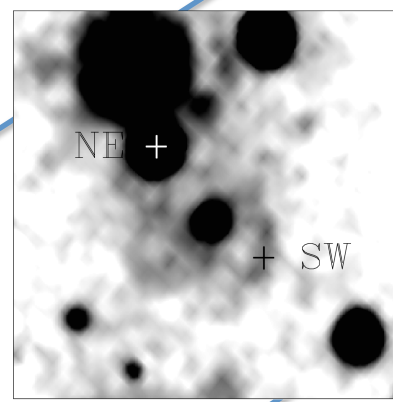
=> **OPR≈3**

- <u>Neufeld et al. 2015</u>: ortho-H_2Cl^+ (2_{12}- 1_{01}) in foreground of diffuse gas toward G29.96-0.02, W51, W3(OH) and W49N, with additional para-H_2Cl^+ (1_{11}- 0_{00}) => **2.5 ≤ OPR ≤ 3**

H_2Cl^+ OPR at z=0.89 toward PKS-1830-211



Lensed blazar
@ z=2.5



Foreground nearly face-on spiral galaxy @ z=0.89

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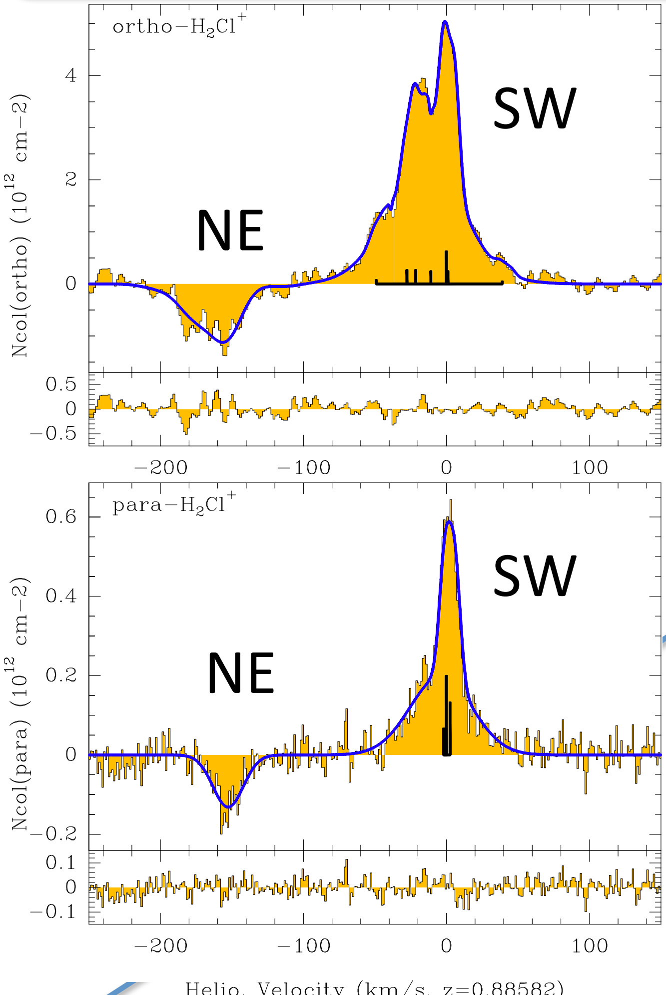

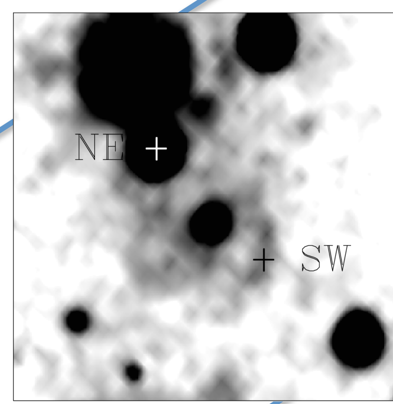

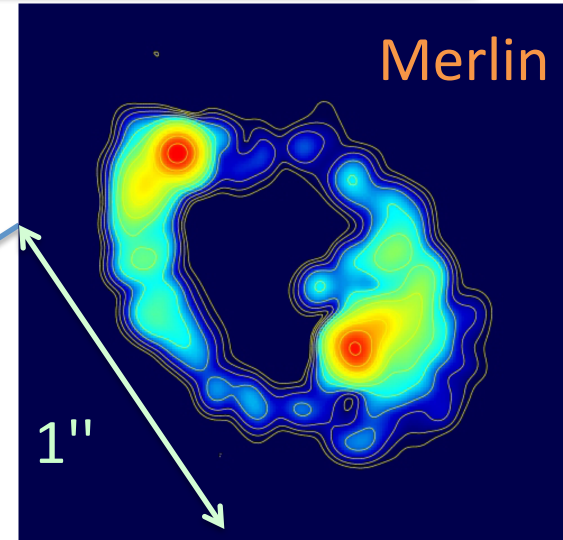

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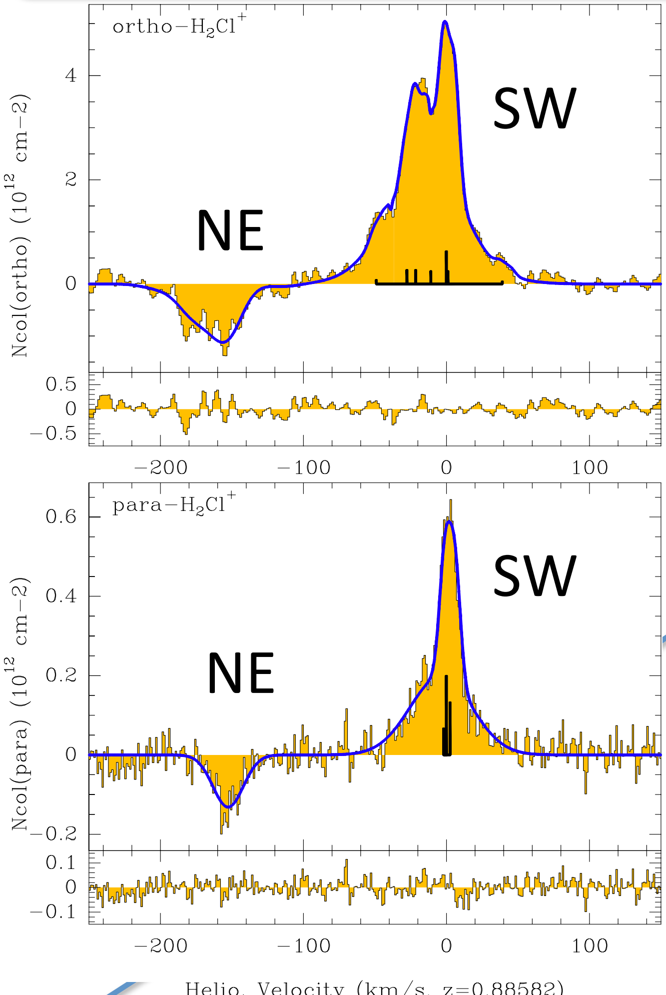
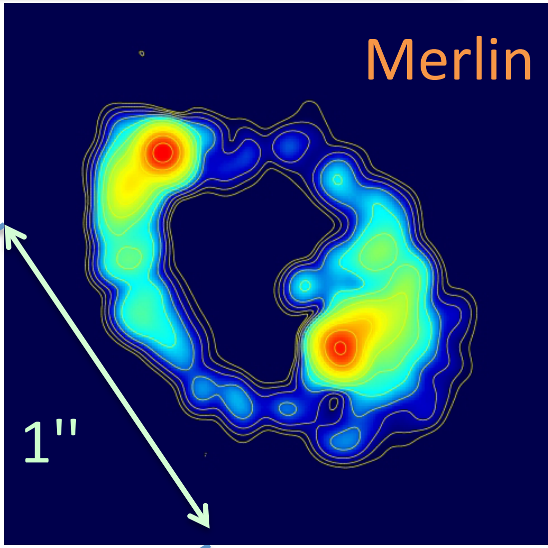
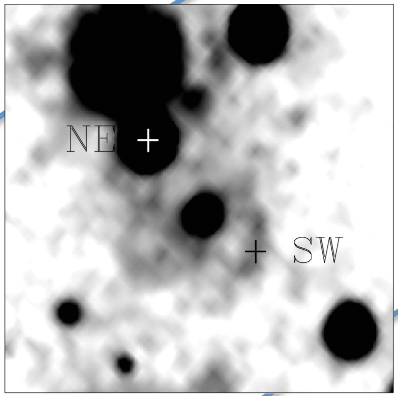


⇒ SW: **OPR≈3 ± 0.13**
⇒ NE: **OPR≈3 ± 0.5**





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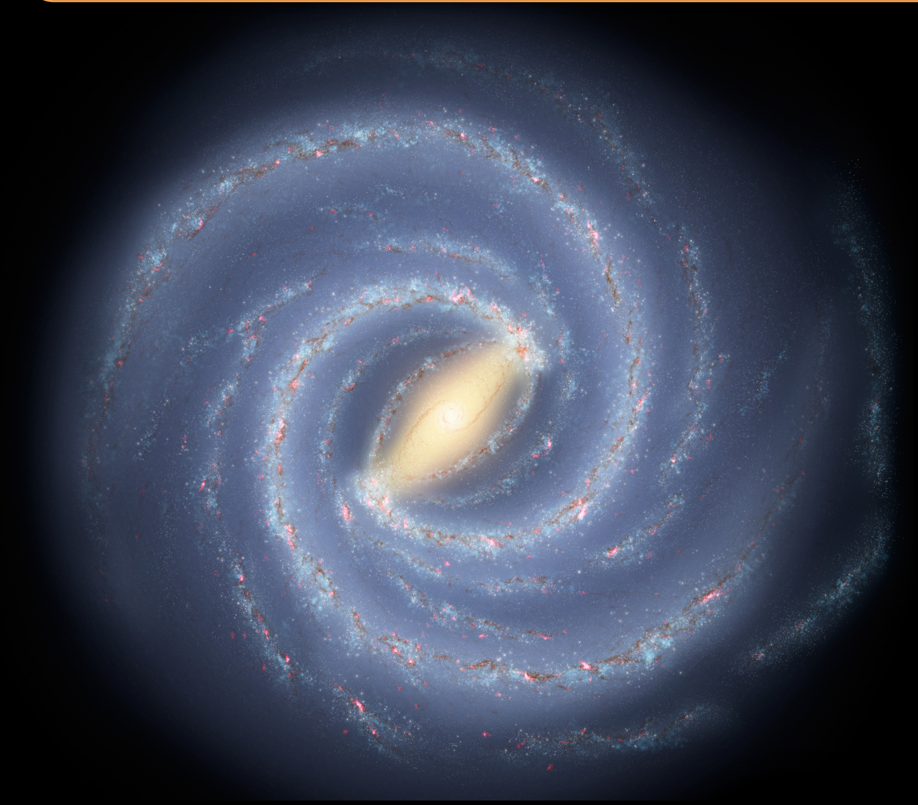
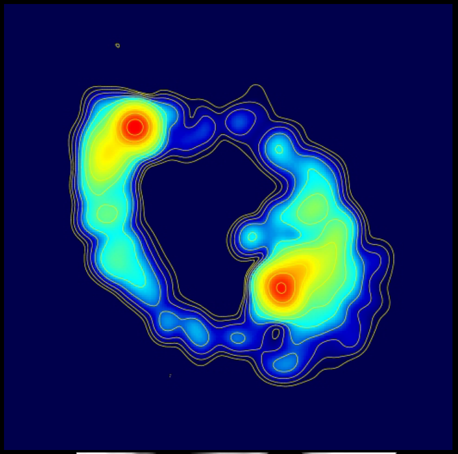
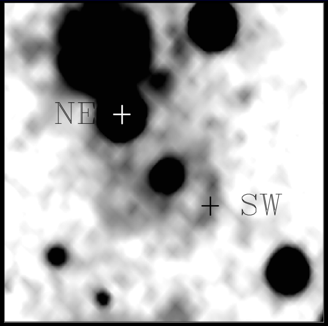
Le Gal et al., in prep.

Interpretation of the observations







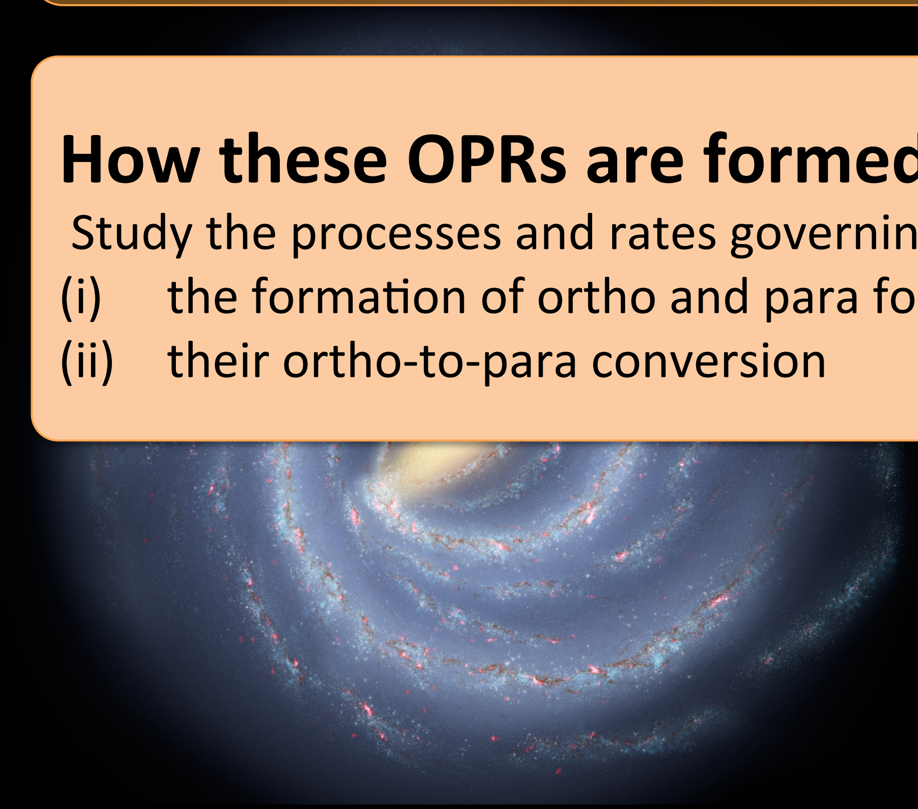
Interpretation of the observations

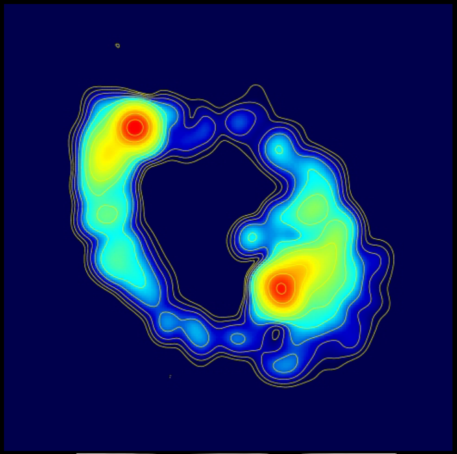
How these OPRs are formed

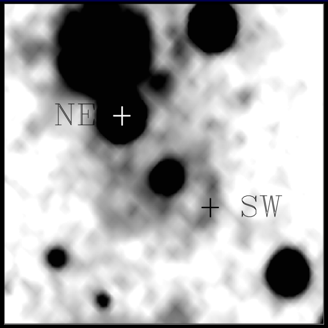
Study the processes and rates governing:

(i) the formation of ortho and para forms

(ii) their ortho-to-para conversion







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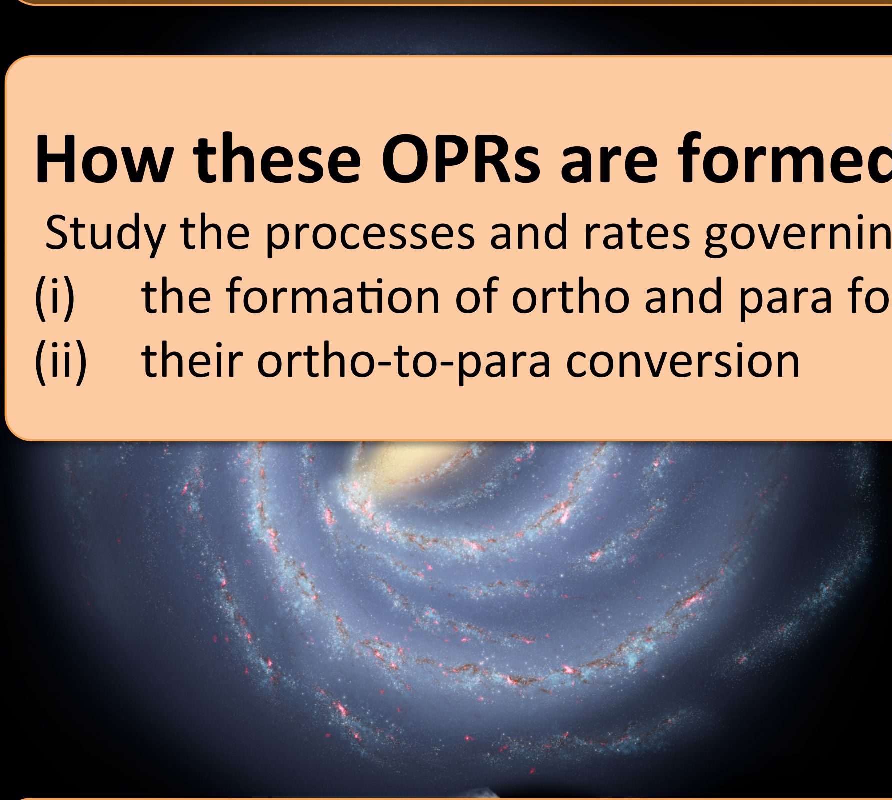

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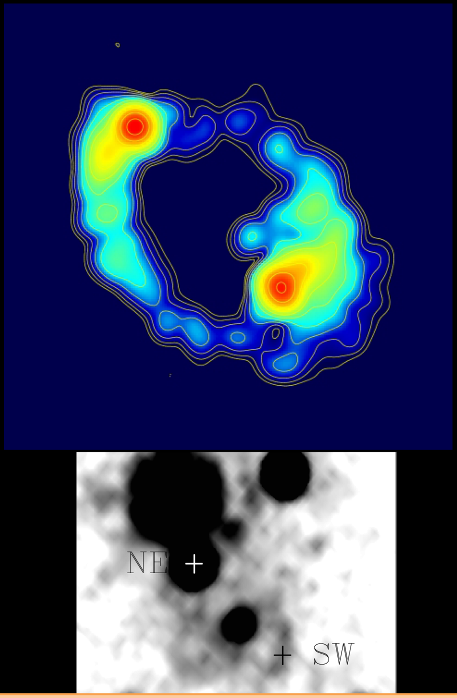


Strategy

Identifying the species and pivotal processes at stake

→ modeling the interstellar chemistry

Astrochemical modeling

- **Context: observations and interests**
  - ortho-to-para ratio (OPR) in the interstellar medium (ISM)
  - The NH_2 and H_2Cl^+ cases
- **Astrochemical modeling**
  - Building chemical network
  - Results: comparison with observations

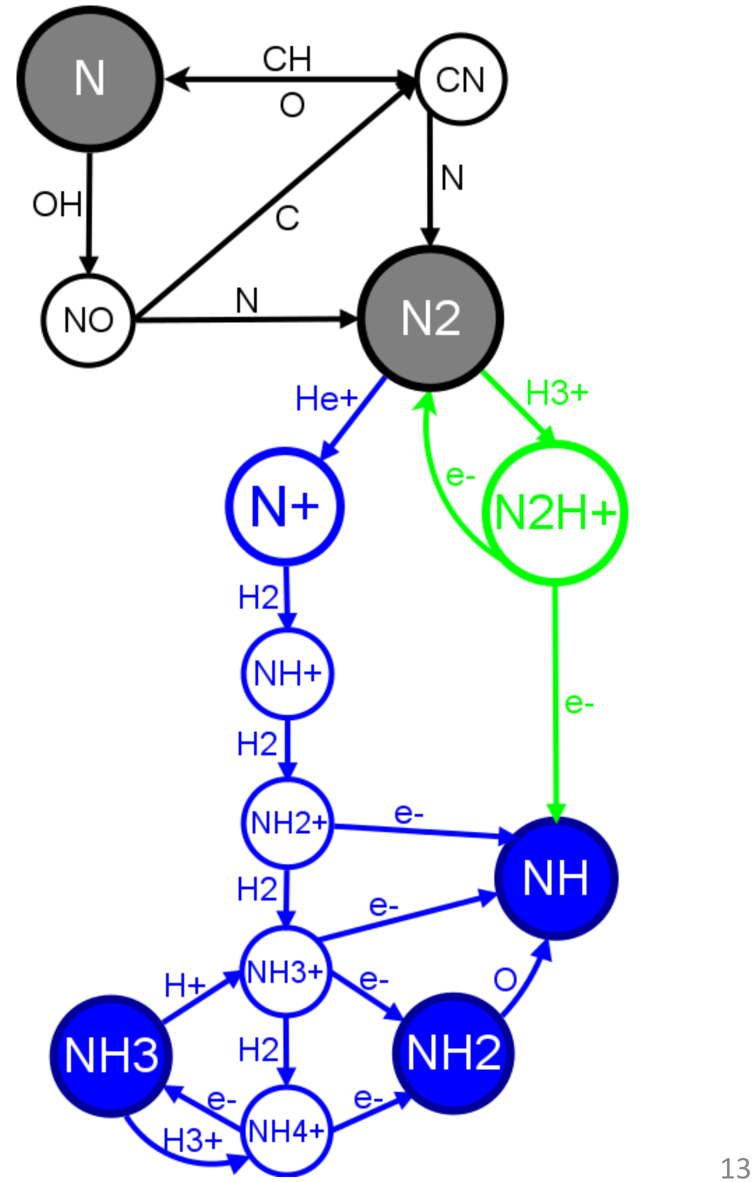
Building chemical network

- Aims:
  - Distinguish ≠ spin configurations of H_2 and multi-hydrogenated species

  ⇒ Update & upgrade of Flower et al. 2006 with rigorous nuclear-spin selection rules (Oka 2004)

  - Based on recent experimental and theoretical work

  ⇒ Rist et al., *JPCA* 2013, Faure et al., *ApJ* 2013 & Le Gal et al., *A&A* 2014



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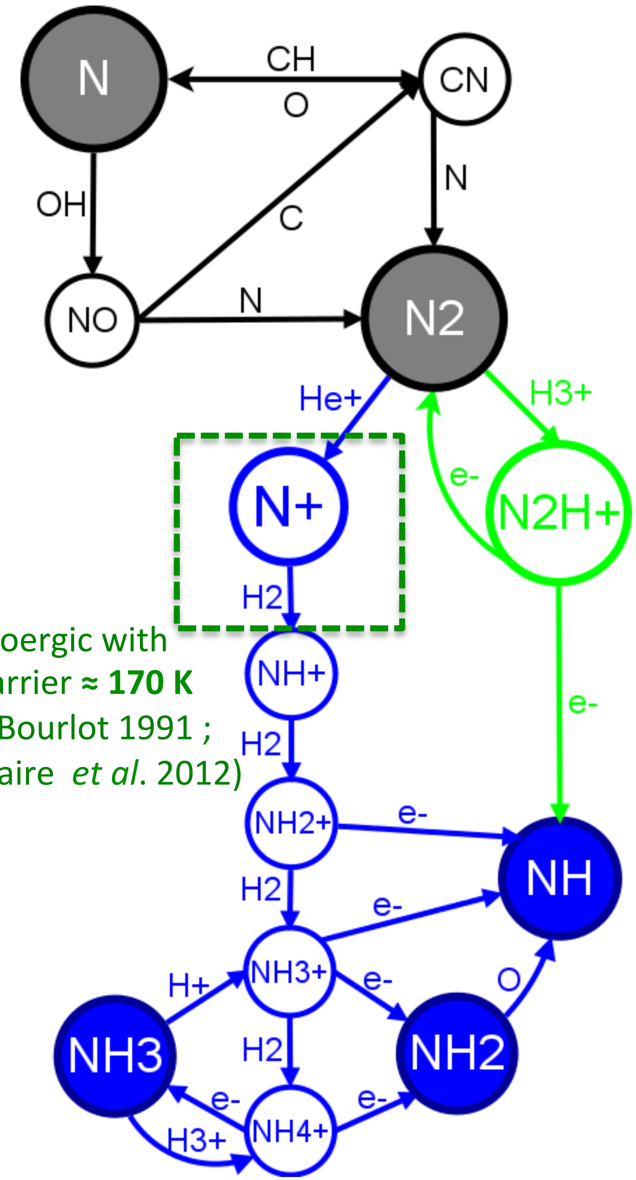
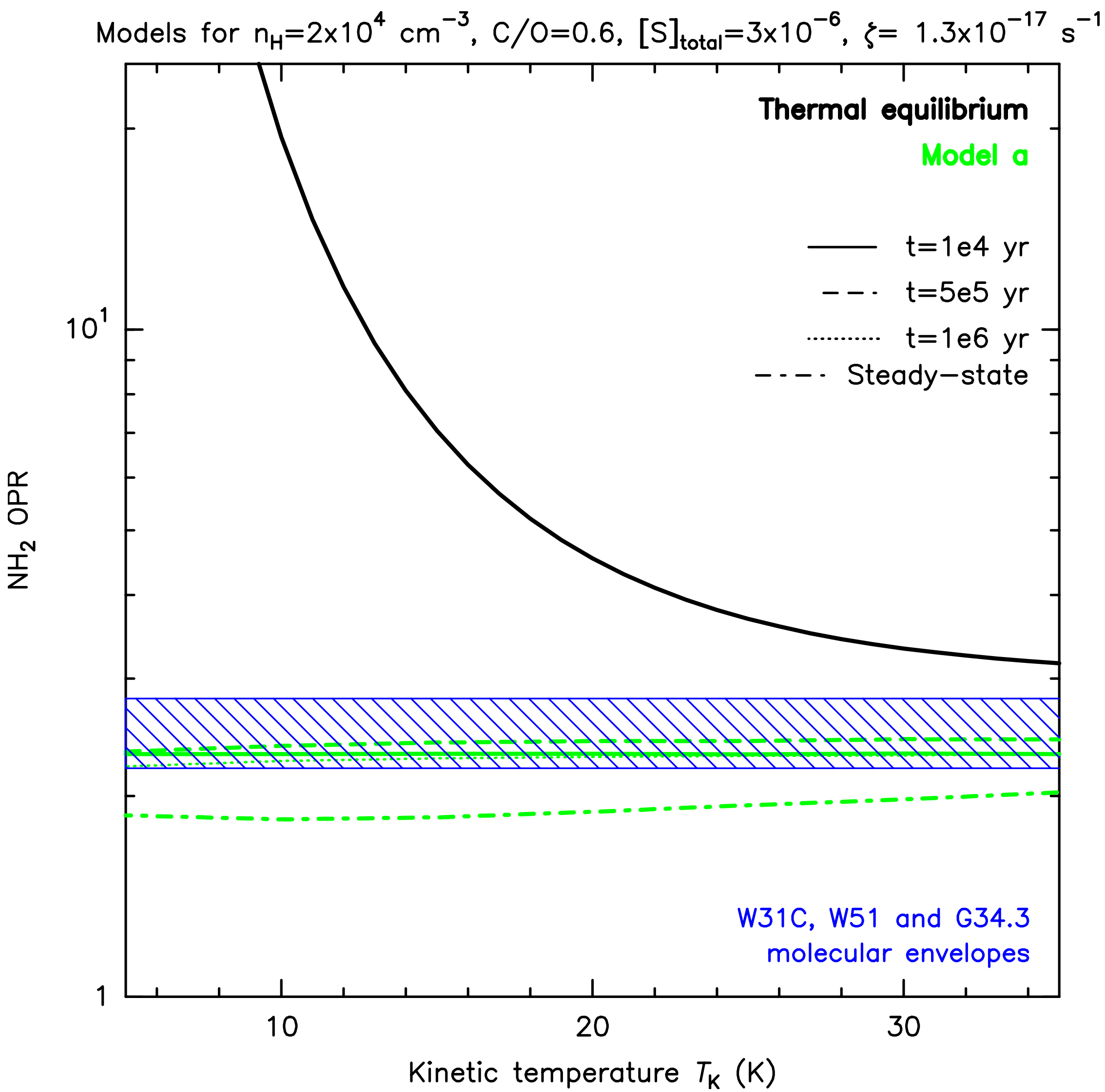


Endoergic with a barrier ≈ **170 K** (Le Bourlot 1991 ; Dislaire *et al*. 2012)

Results: NH_2 OPR with T



Persson, Olofsson, ***Le Gal*** *et al., A&A. (2016)*

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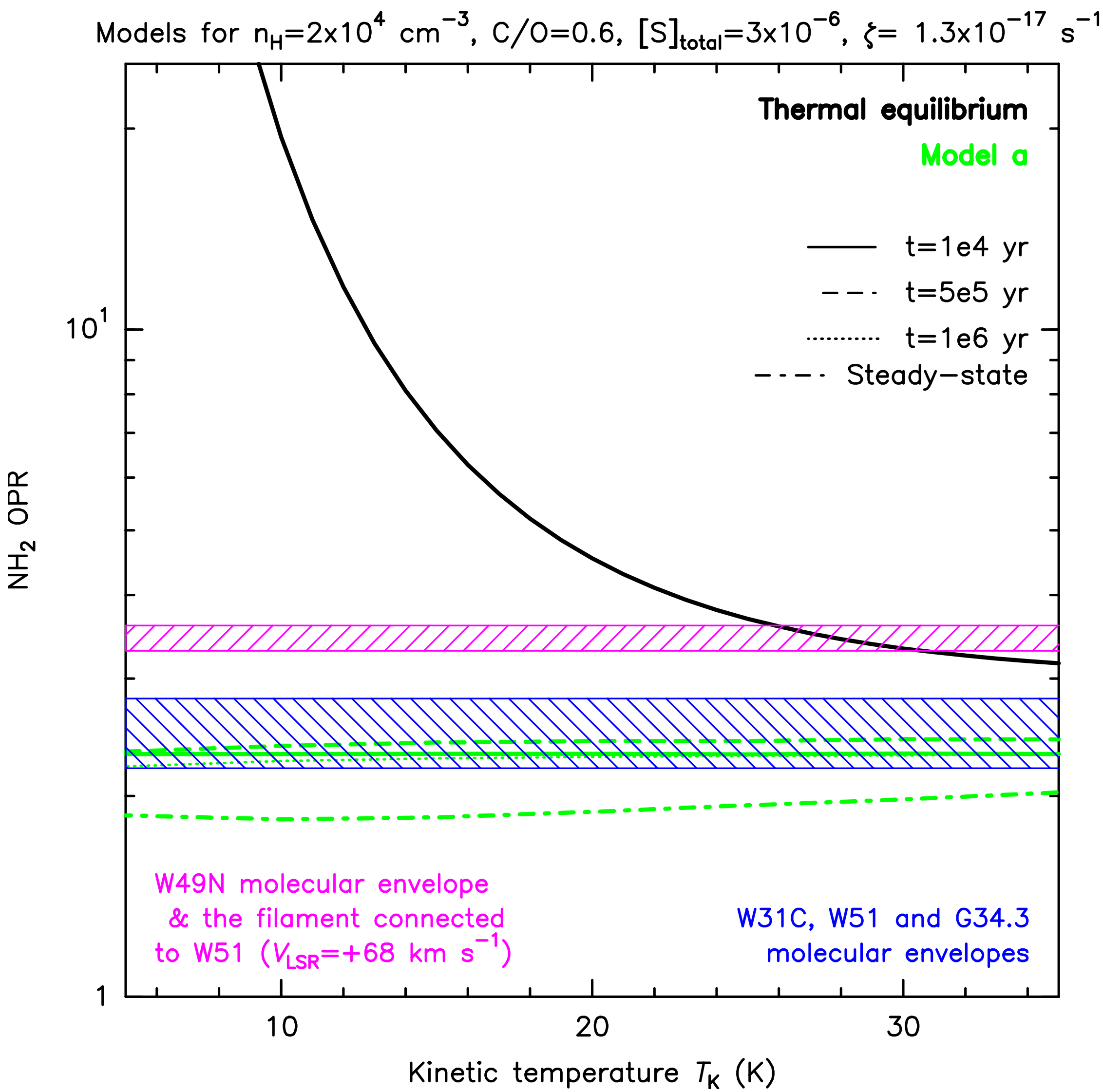

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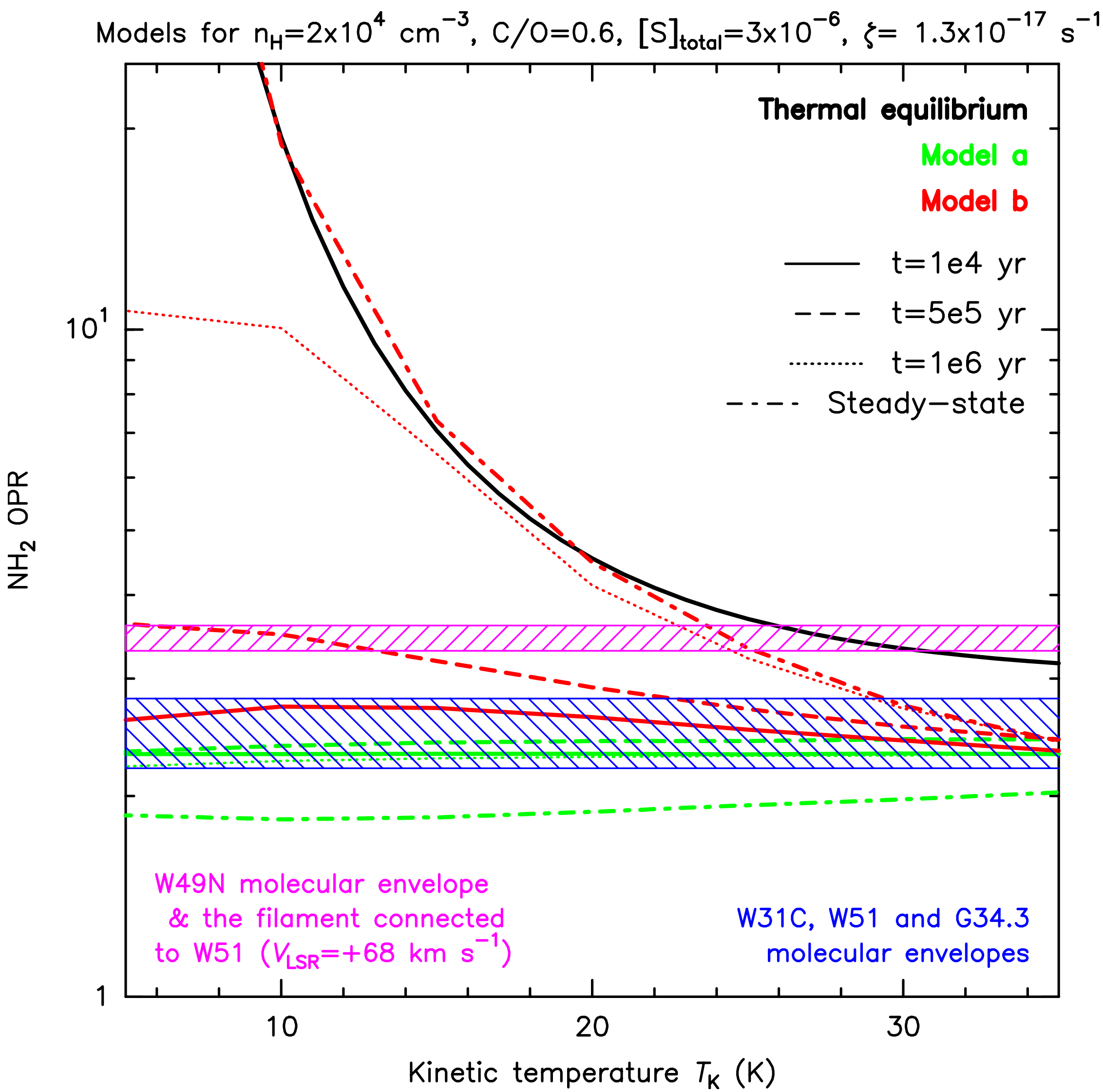

- New mechanism to allow OPR relaxation:

  $\Rightarrow$ H + NH_2 H-exchange

$$\mathrm{H} + \mathrm{o{-}NH_2} \xrightarrow{k_{o\to p}} \mathrm{H} + \mathrm{p{-}NH_2}$$

$$\mathrm{H} + \mathrm{p{-}NH_2} \xrightarrow{k_{p\to o}} \mathrm{H} + \mathrm{o{-}NH_2}$$

with $k_{o\to p} = k_{p\to o} \exp(-30.4/T)\,\mathrm{cm^3\,s^{-1}}$

$$k_{p\to o} = 1\times10^{-10}\,\mathrm{cm^3\,s^{-1}}$$

*Persson, Olofsson, **Le Gal** et al., A&A. (2016)*

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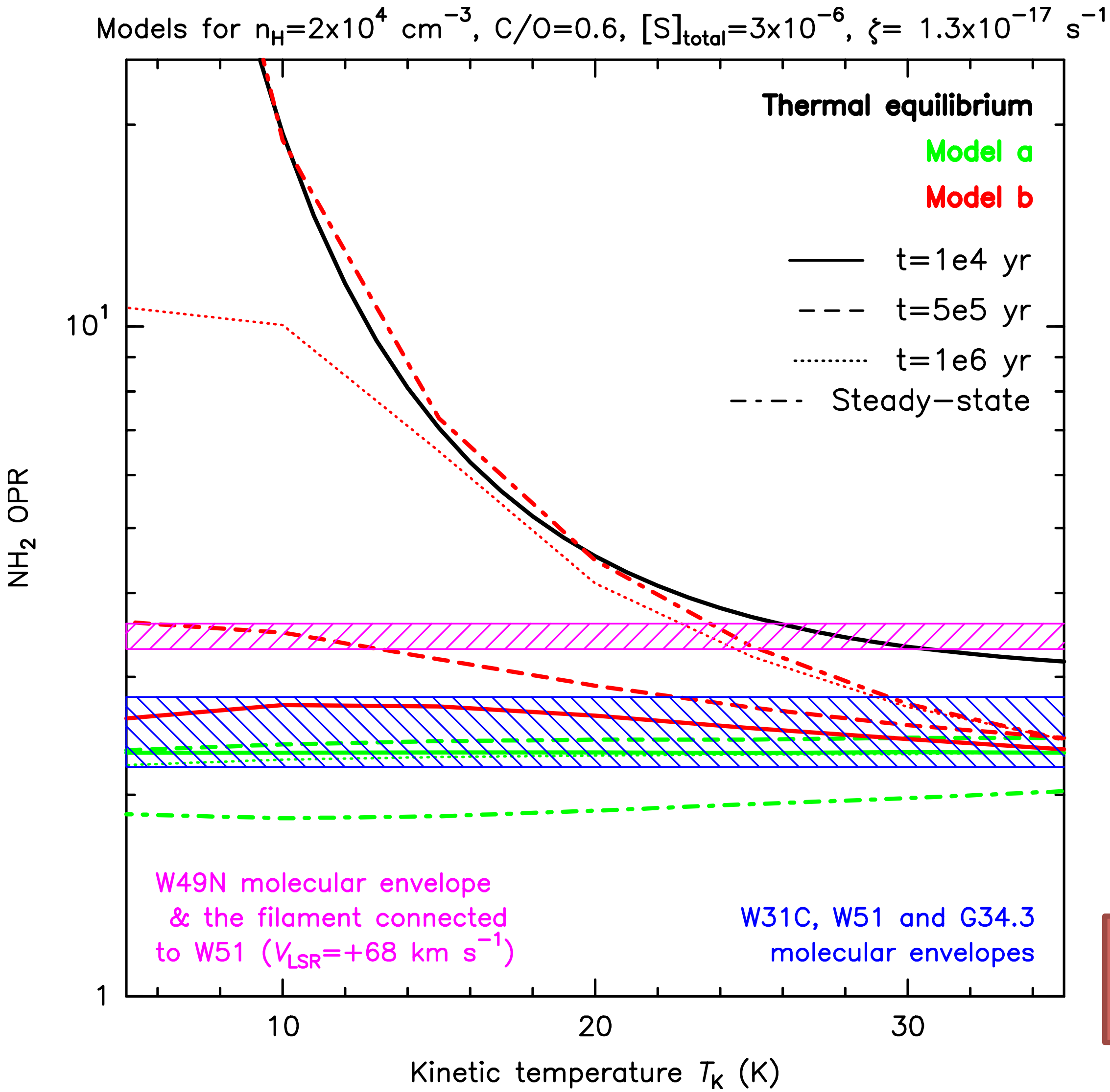

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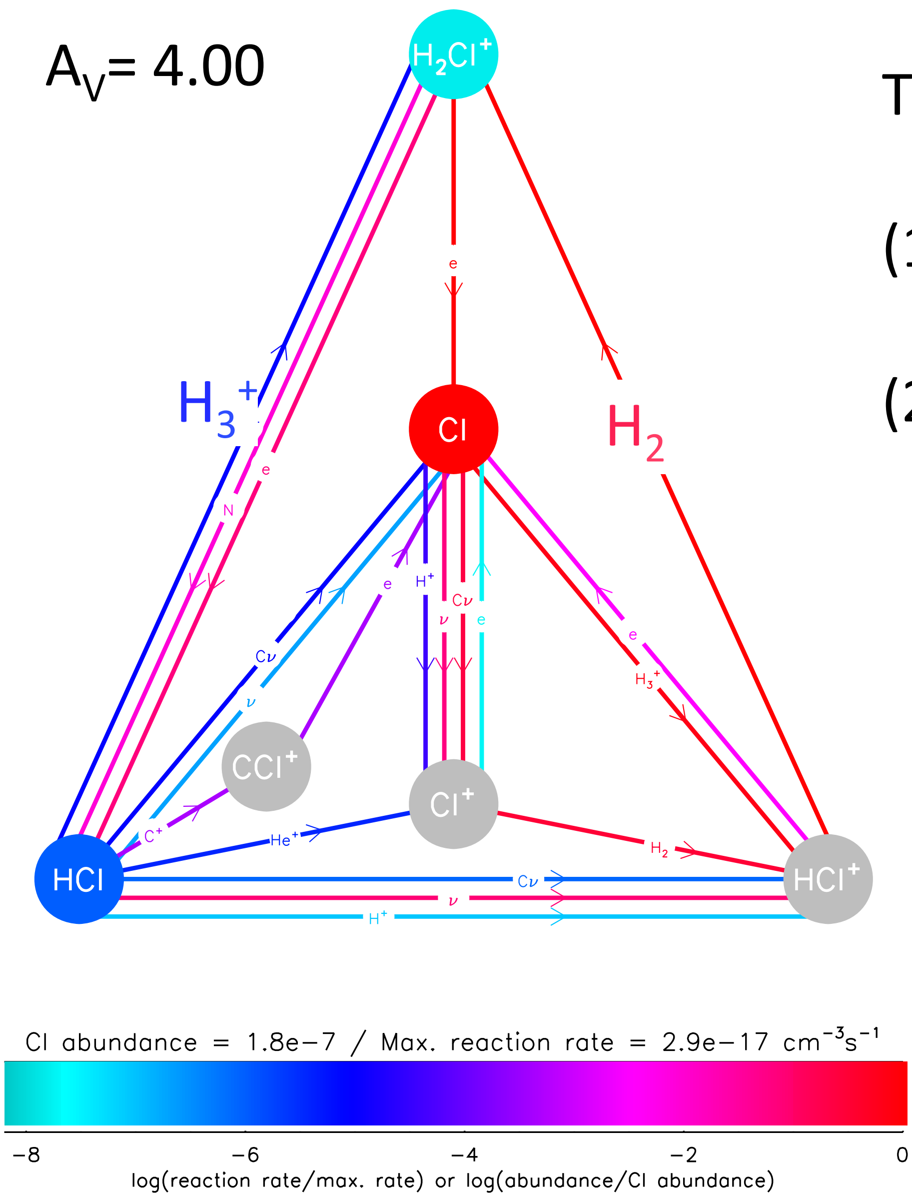
Confirmed to be barrierless
(Le Gal et al., A&A 2016)

*Persson, Olofsson, **Le Gal** et al., A&A. (2016)*

H_2Cl^+ chemistry



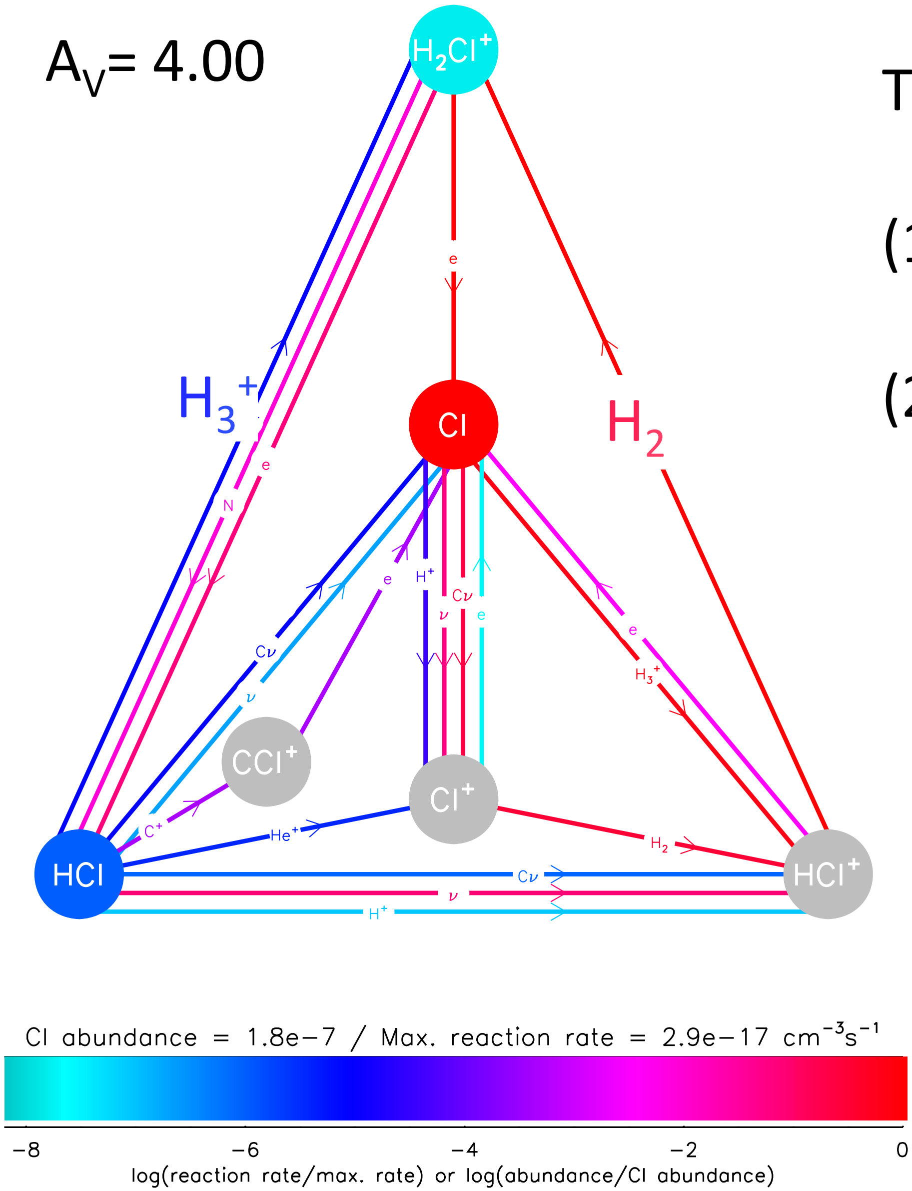
Two main H_2Cl^+ formation pathways:

(1) $H_2 + HCl^+ \rightarrow H_2Cl^+ + H$

(2) $H_3^+ + HCl \rightarrow H_2Cl^+ + H_2$

Neufeld & Wolfire, ApJ (2009)

H_2Cl^+ chemistry



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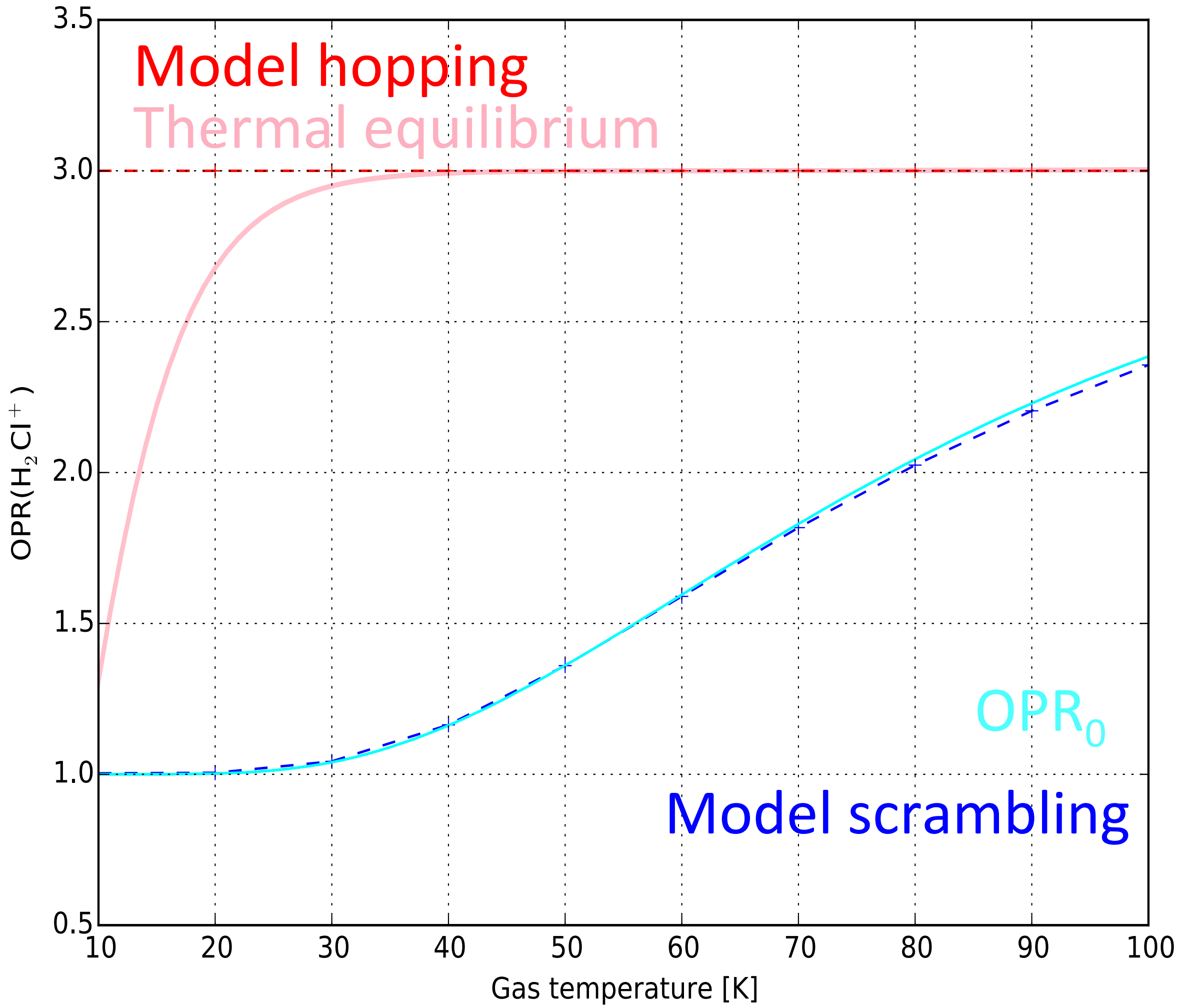
H_2Cl^+ OPR formation?
Full scrambling? Hopping?

Neufeld & Wolfire, ApJ (2009)

H_2Cl^+ OPR: full scrambling *vs* hopping (I)



Le Gal et al., in prep.

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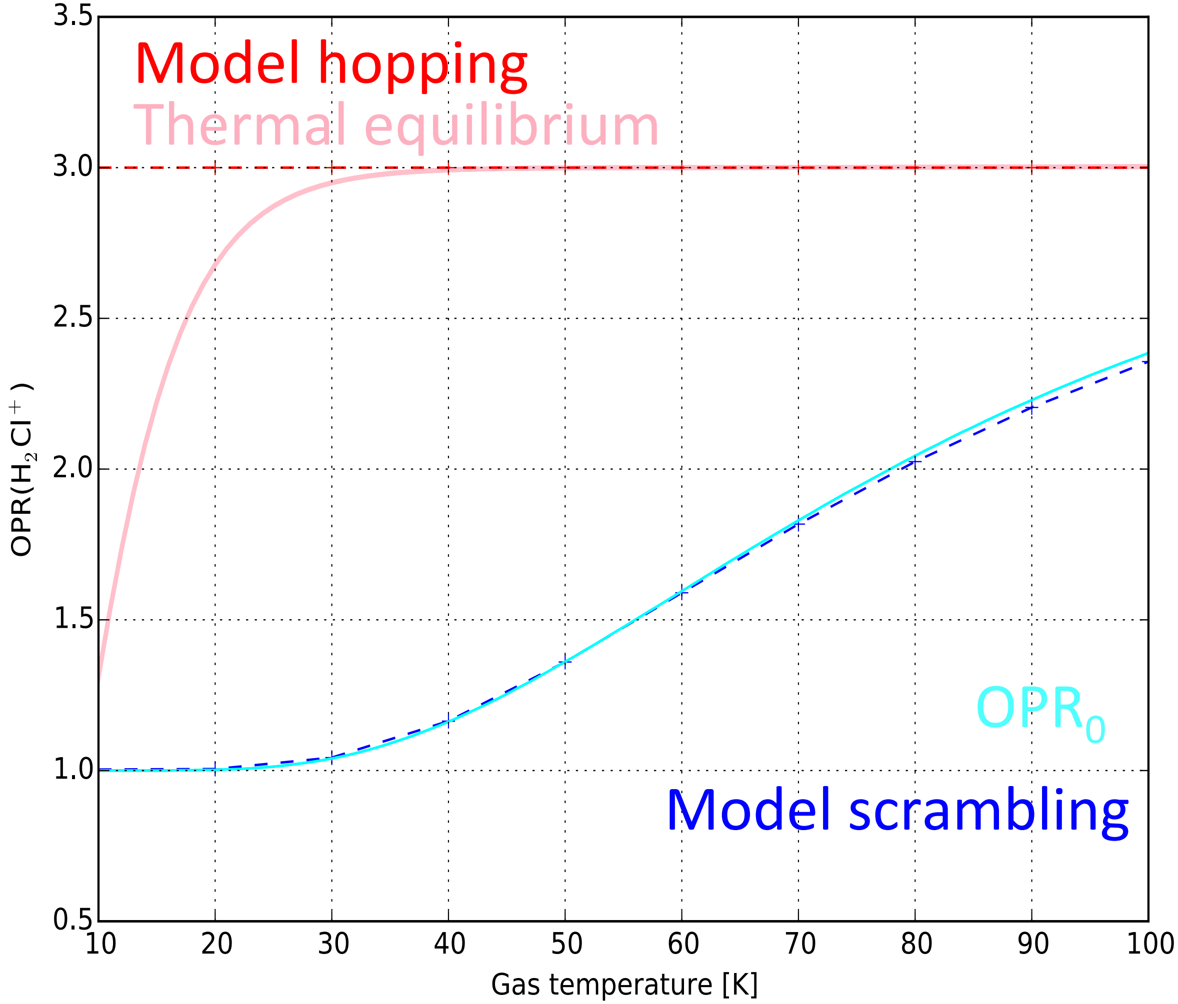


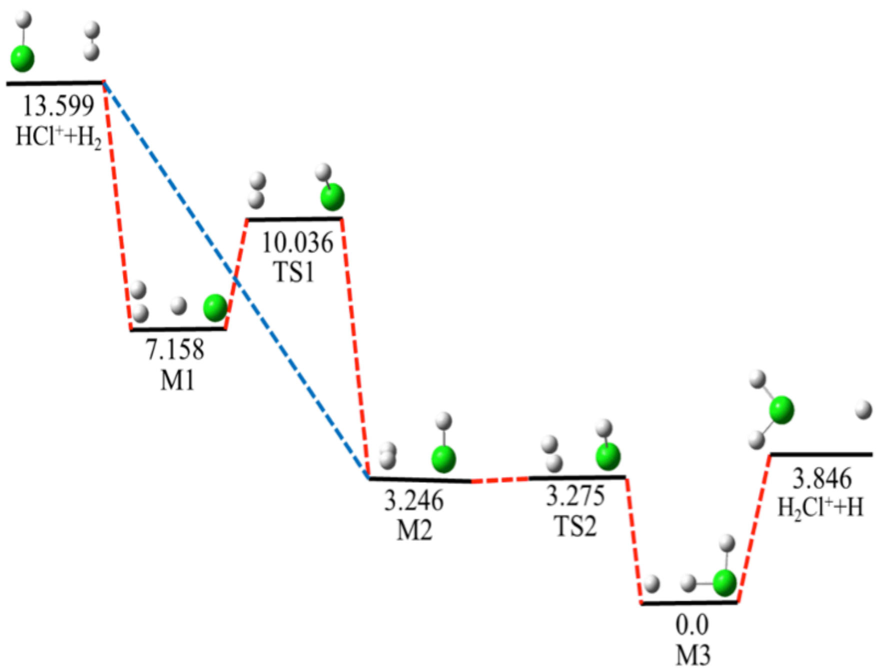
$H_2 + HCl^+ \rightarrow H_2Cl^+ + H$

$$\mathrm{OPR}_0\left(\mathrm{H_2Cl^+}\right) = \frac{5\ \mathrm{OPR}\left(\mathrm{H_2}\right) + 3}{\mathrm{OPR}\left(\mathrm{H_2}\right) + 3}$$

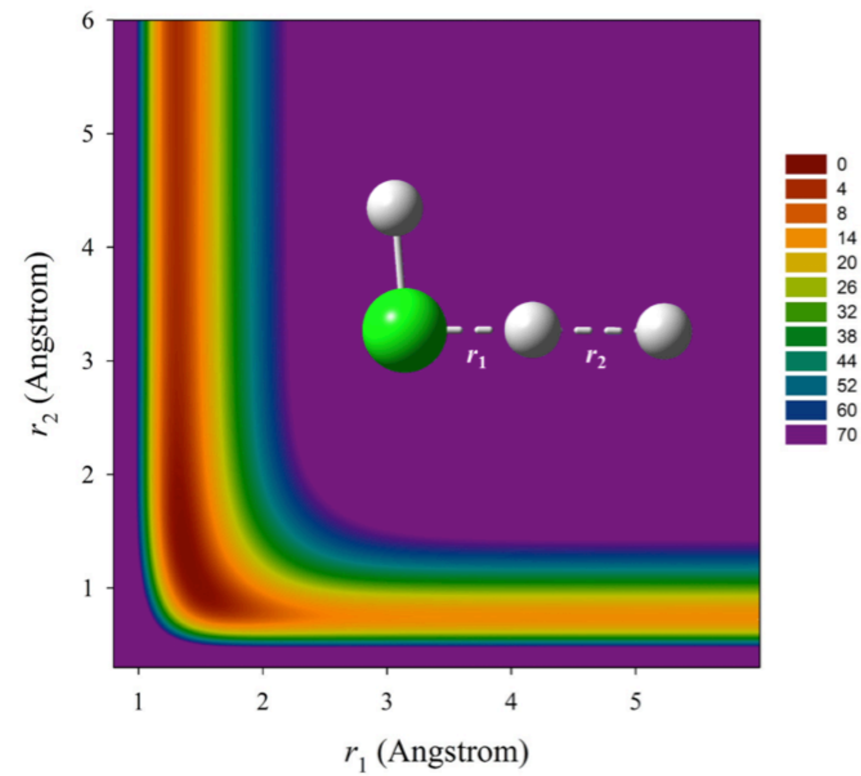
Le Gal et al., in prep.

Quasi-classical trajectory calculations

$H_2 + HCl^+ \rightarrow H_2Cl^+ + H$



Energy profil with energies in kcal/mol relative to the global minimum M3



Contour plot for the H atom hopping reaction process

Le Gal et al., in prep.

H_2Cl^+ OPR thermalization reaction?

$o\text{-}H_2Cl^+ + H$ <-> $p\text{-}H_2Cl^+ + H$?

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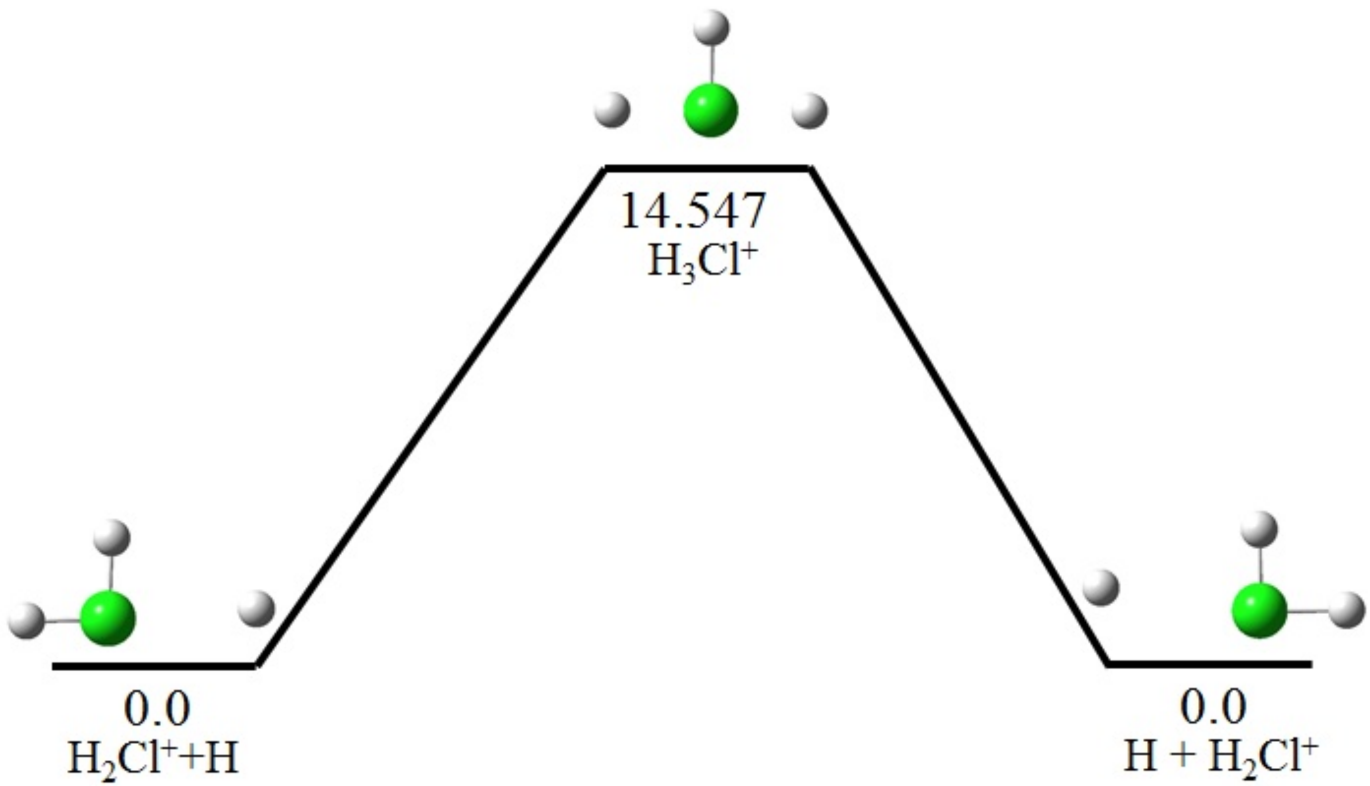

Le Gal et al., in prep.

Conclusions & future works

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- **Gas-phase spin chemistry** reproduce:
  - interstellar NH_2 OPR in cold gas:
    full scrambling selection rules for OPR < 3
    & H-exchange reaction for OPR > 3
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    only hopping mechanism for OPR = 3
- Models predictions with full scrambling selection rules:
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Future works:

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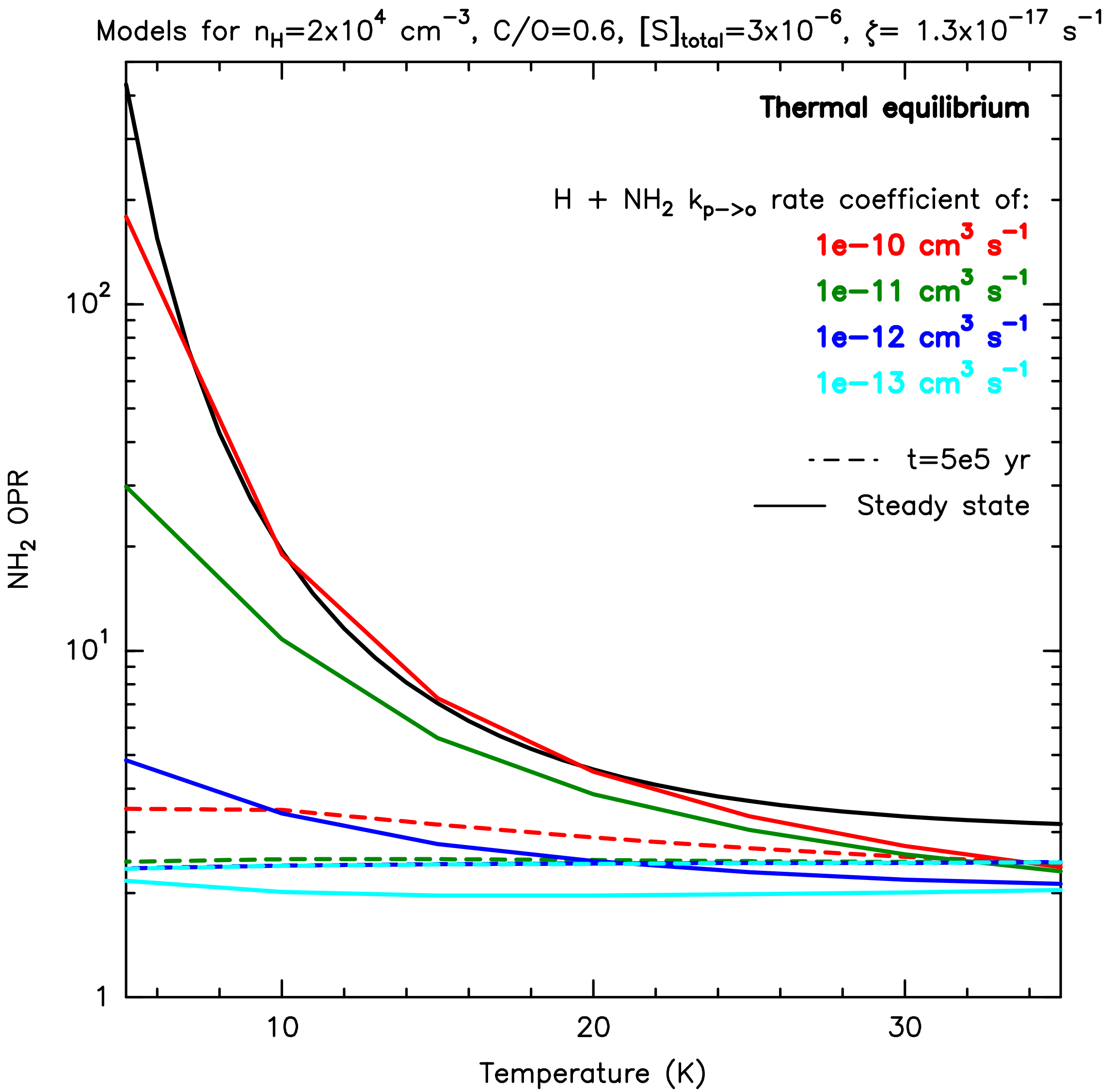
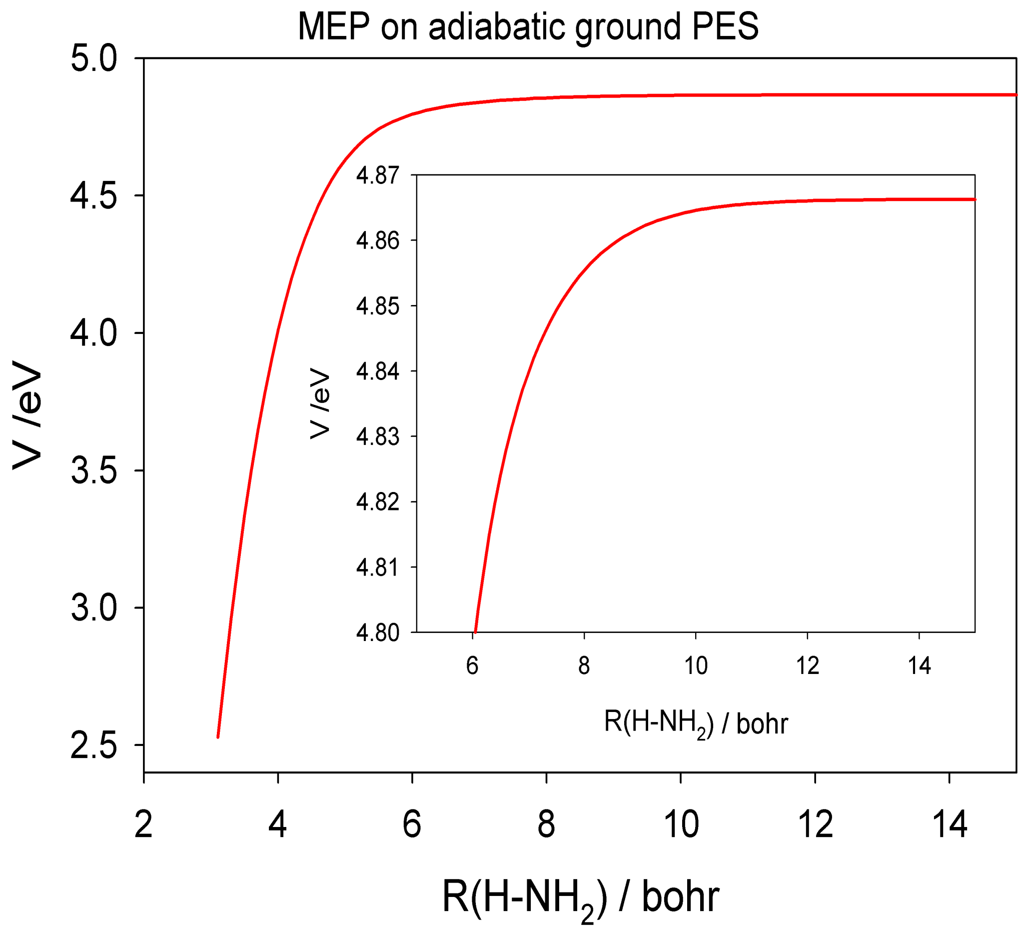
Thanks for your attention!

Influence of the rate coefficient



Le Gal et al., A&A. (2016)

Results: H + NH_2 H-exchange barrierless

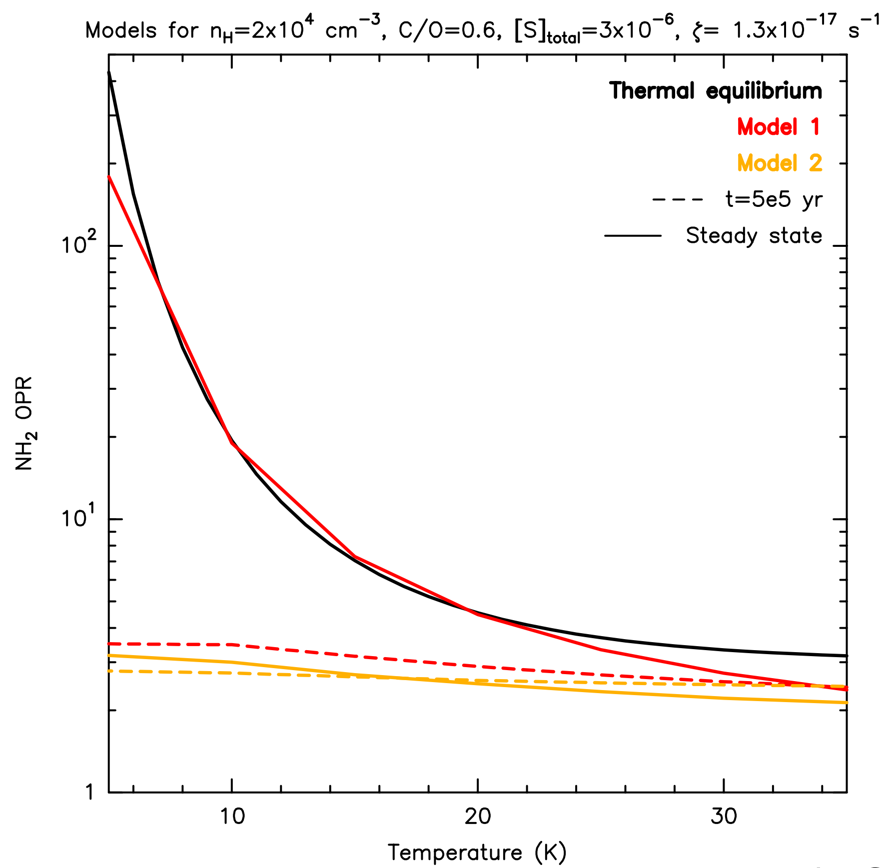


Le Gal et al., A&A. (2016)

H + NH_2 H-exchange rate coefficient of ≈10^{-10} cm^3 s^{-1} is consistent with the theoretical computations

Impact of NH_2 chemistry updates

Chemical reactions[a]						α ($cm^3\ s^{-1}$)	β	γ	References
NH_2	N	→	N_2	H	H	1.2(-10)	0.00	0.00	KIDA[b]
NH_2	O	→	NH	OH		7.0(-12)	-0.1	0.00	KIDA[c]
						3.5(-12)	0.5	0.00	Le Gal et al. (2014a)[d]
NH_2	O	→	HNO	H		6.3(-11)	-0.1	0.00	KIDA[c]



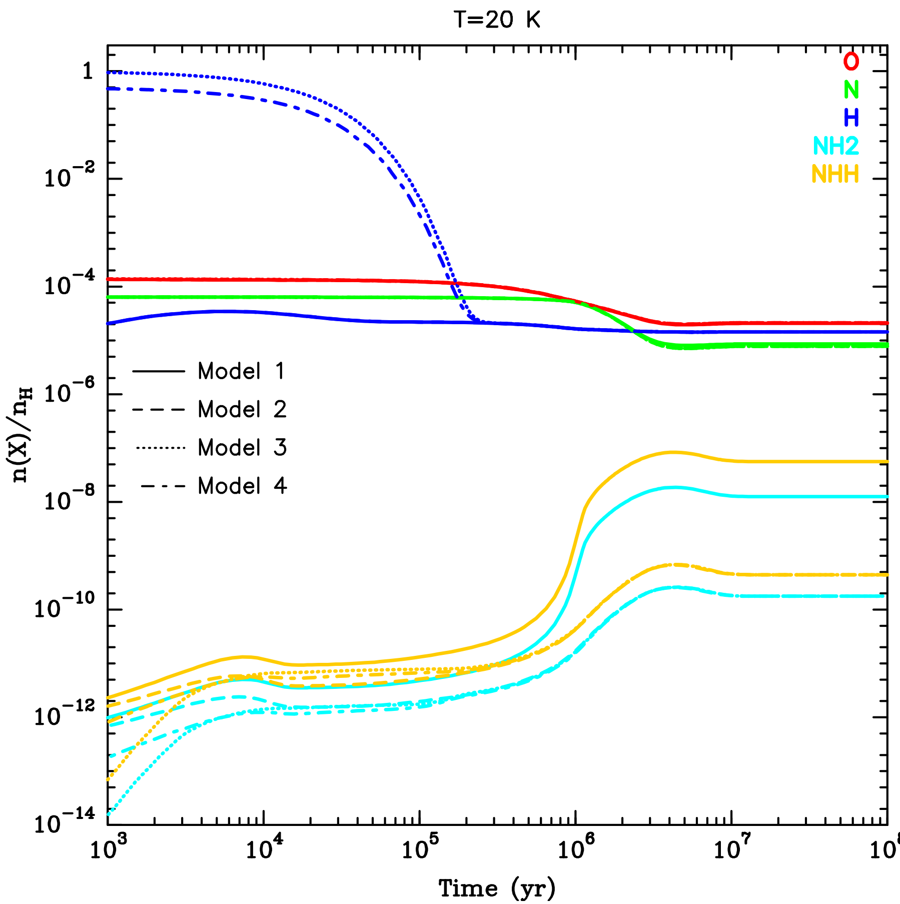
Le Gal et al., A&A. (2016)

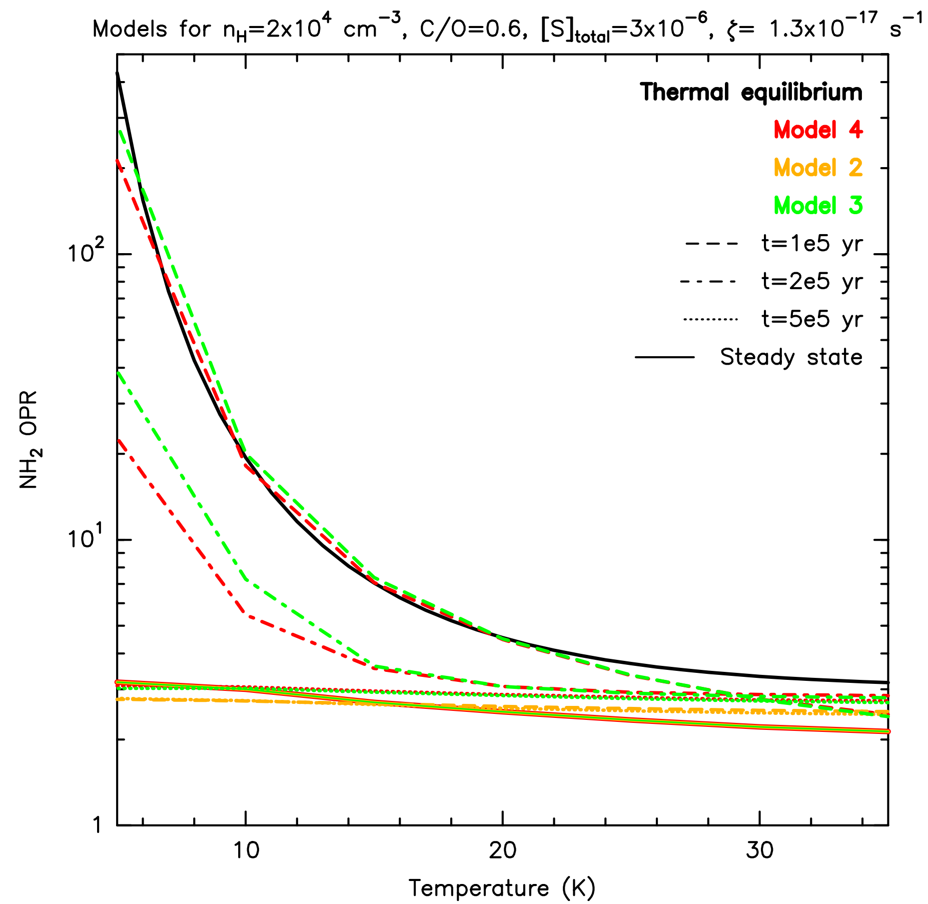
Further modeling study

Modifications \ Models	1	2	3	4	5
H + NH_2 H-exchange addition (reactions 5 and 6)	X	X	X	X	X
NH_2 destruction updates (see Table 2)		X	X	X	X
$[H_{tot}]_{ini} = 2 \times [H_2]$	X	X			X
$[H_{tot}]_{ini} = [H]$			X		
$[H_{tot}]_{ini} = \frac{1}{2} \times [H] + [H_2]$				X	
$\zeta = 1.3 \times 10^{-17}\ s^{-1}$	X	X	X	X	
$\zeta = 3 \times 10^{-17}\ s^{-1}$					X
$\zeta = 2 \times 10^{-16}\ s^{-1}$					
$n_H = 2 \times 10^4\ cm^{-3}$	X	X	X	X	X

Le Gal et al., A&A. (2016)

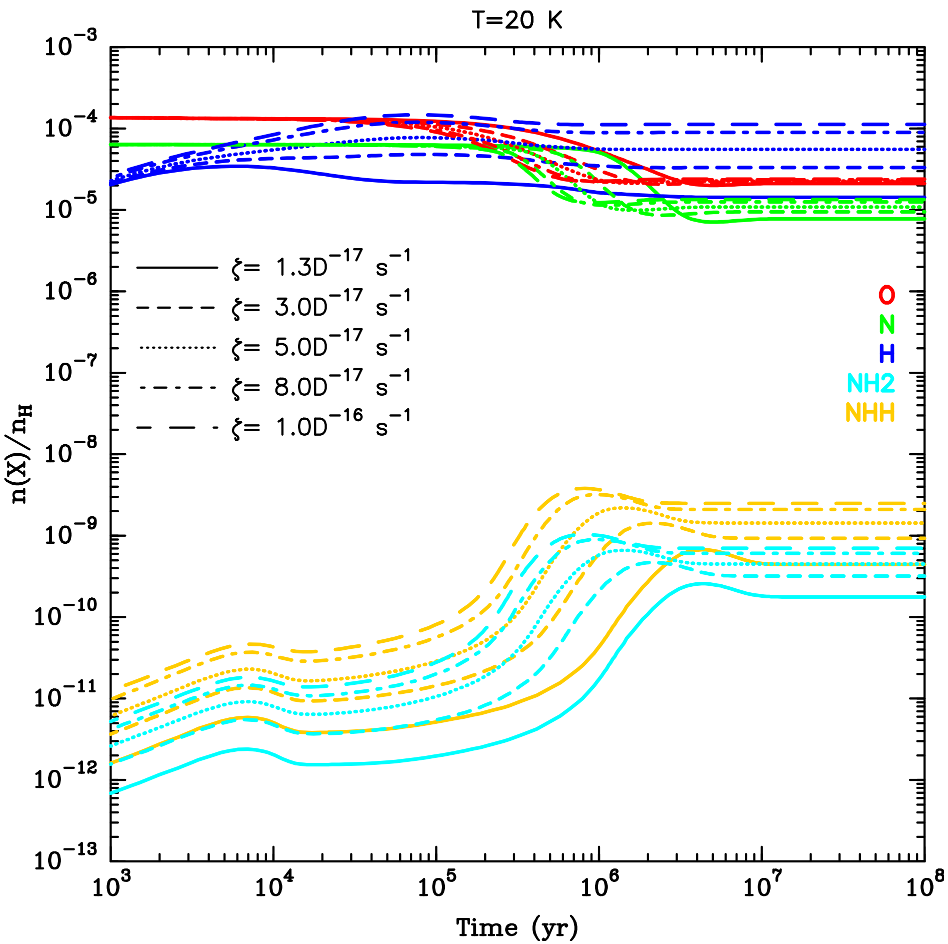
Impact of the initial form of hydrogen

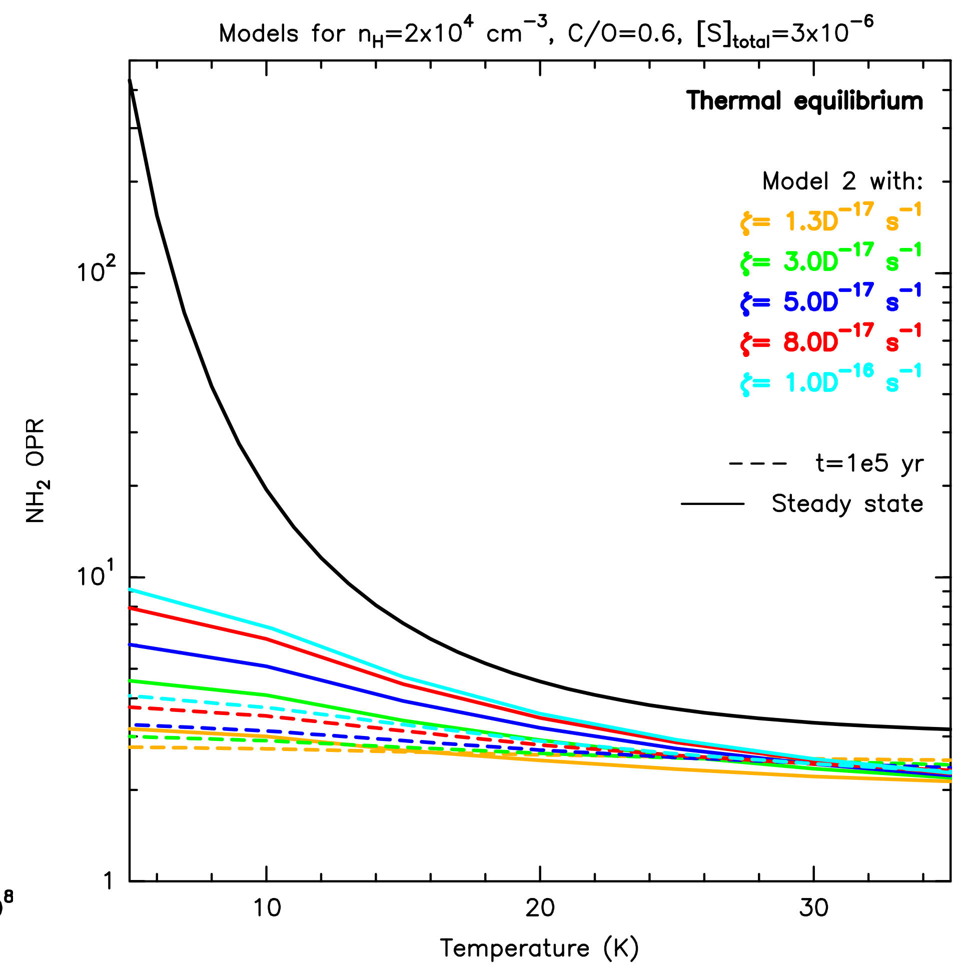




Le Gal et al., A&A. (2016)

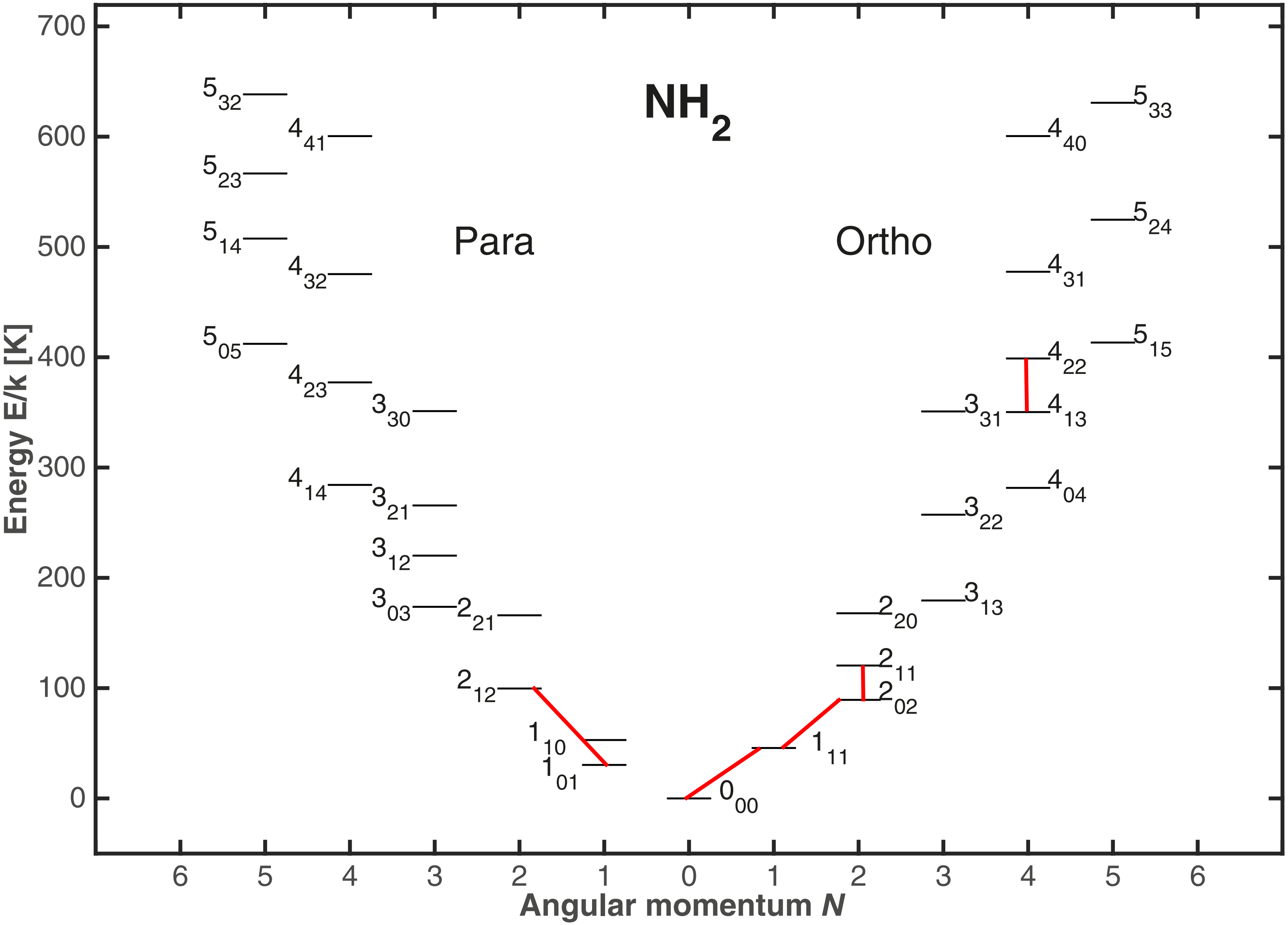
Impact of the ionization rate





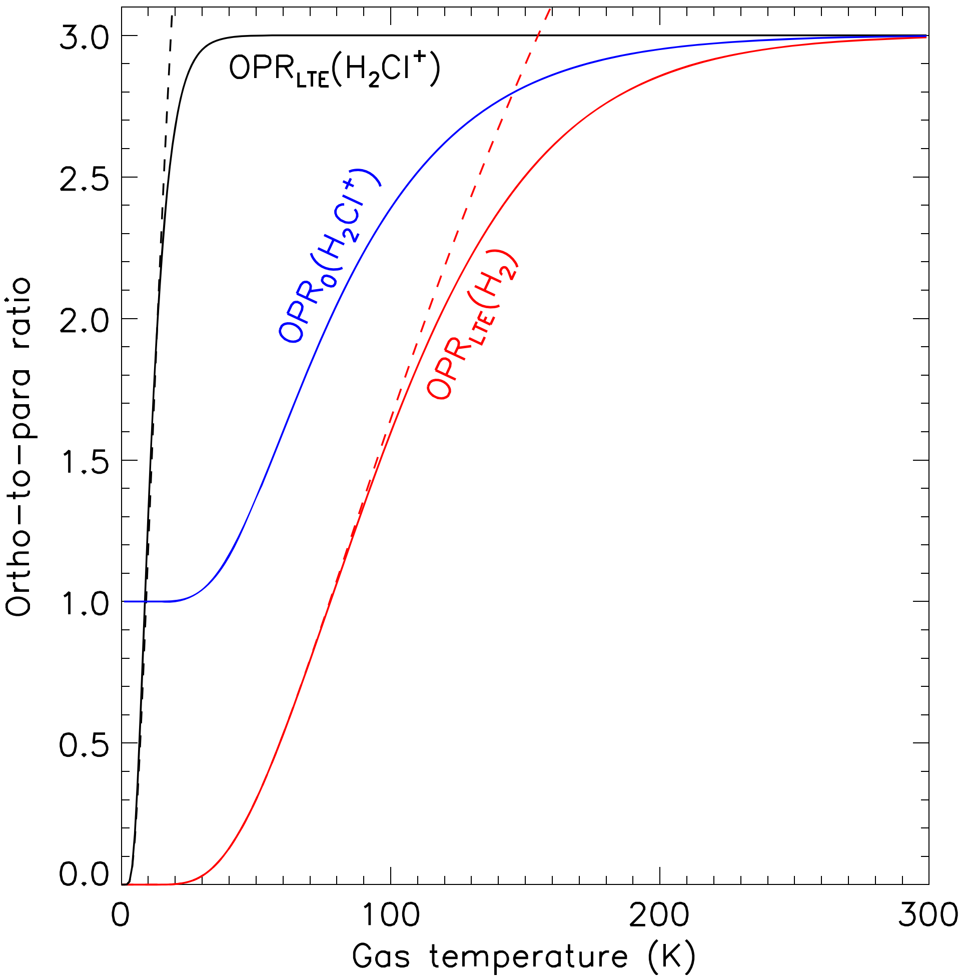
Le Gal et al., A&A. (2016)

Energy level diagram of NH_2



*(Persson, Olofsson, **Le Gal** et al., A&A. 2016)*

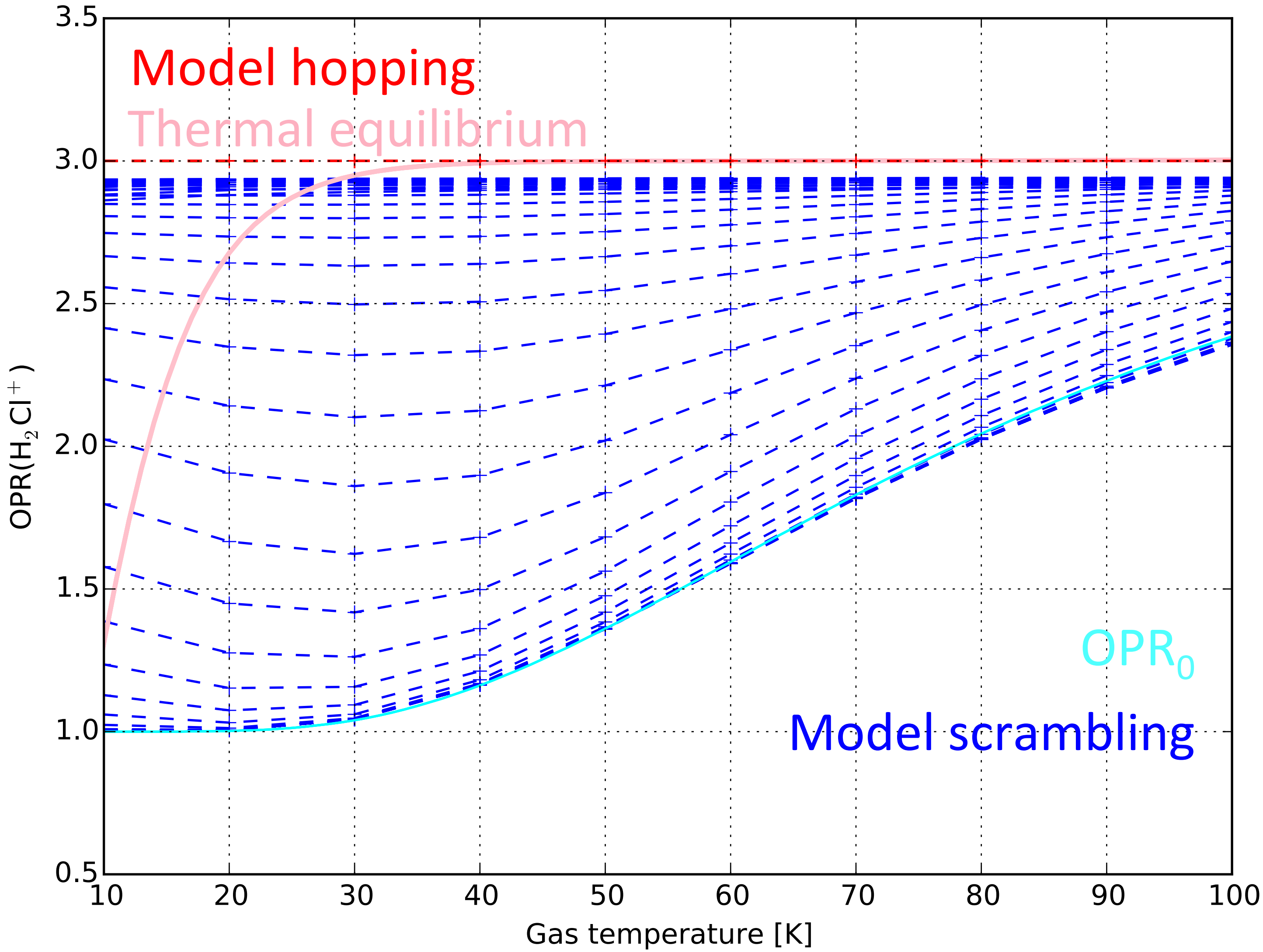
H_2Cl^+ OPR: full scrambling *vs* LTE



$$\mathrm{OPR}_0\left(\mathrm{H_2Cl^+}\right) = \frac{5\ \mathrm{OPR}\left(\mathrm{H_2}\right) + 3}{\mathrm{OPR}\left(\mathrm{H_2}\right) + 3}$$

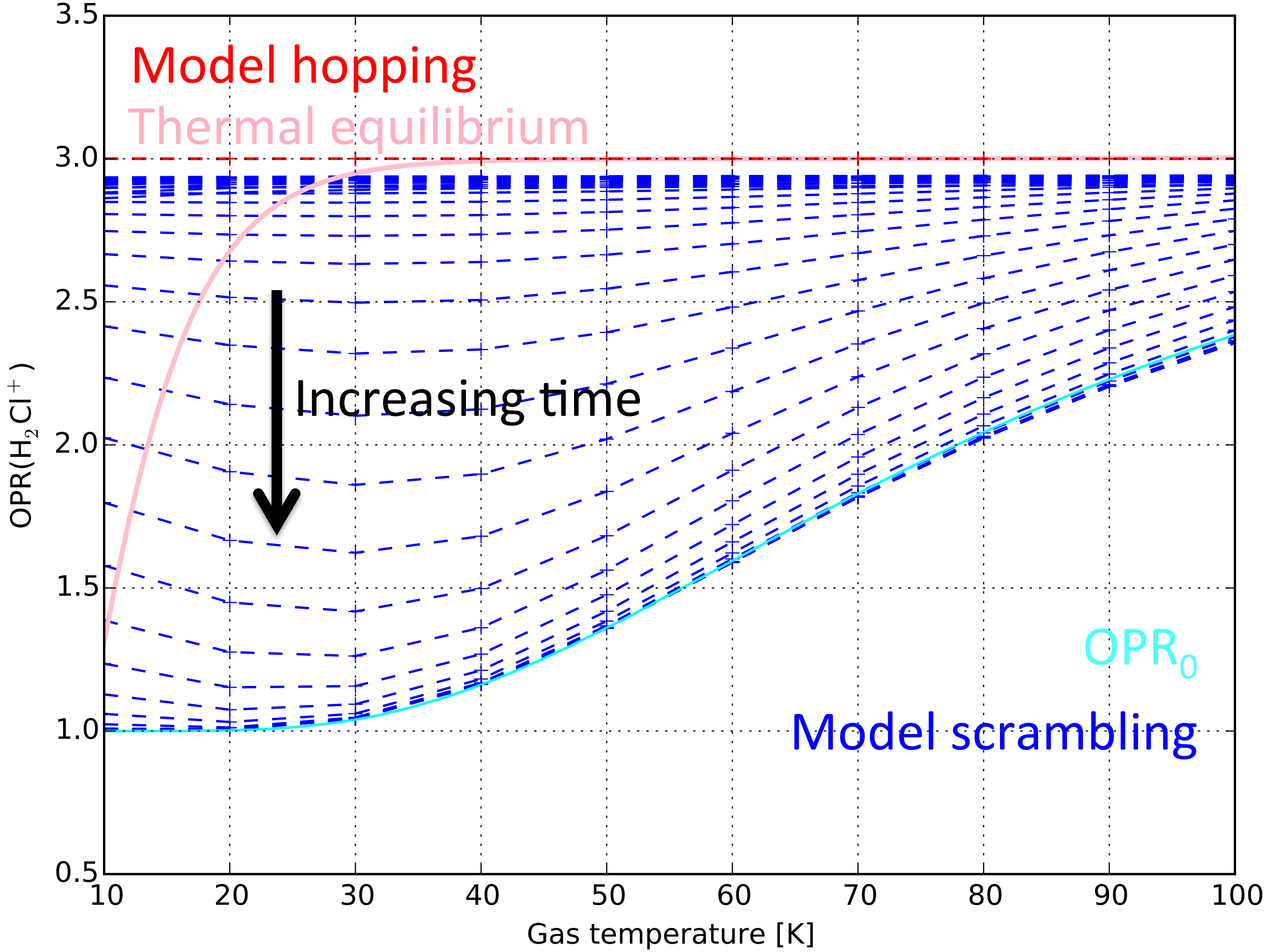
Neufeld et al. ApJ (2015)

H_2Cl^+ OPR: full scrambling *vs* hopping (II)



Le Gal et al., in prep.

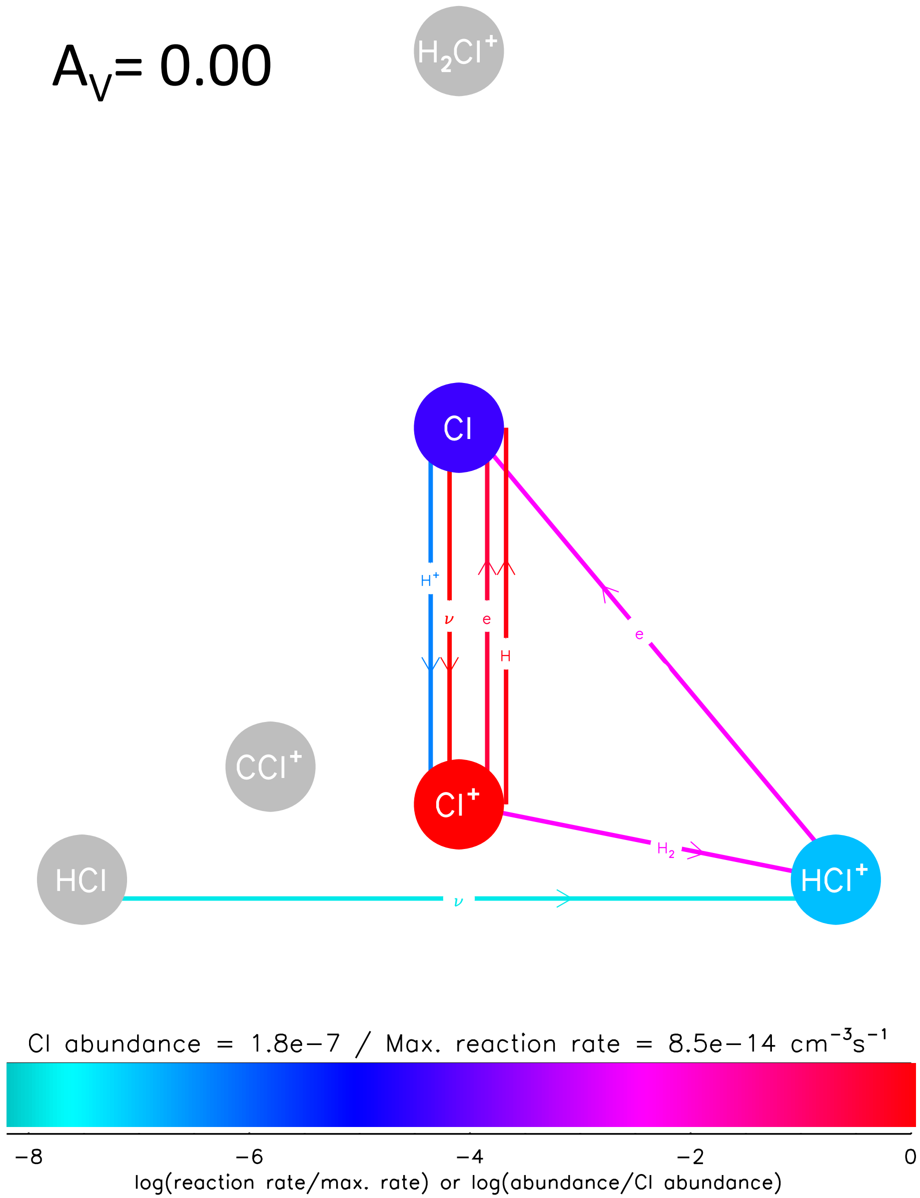
H_2Cl^+ OPR: full scrambling *vs* hopping (II)



Le Gal et al., in prep.

H_2Cl^+ chemistry

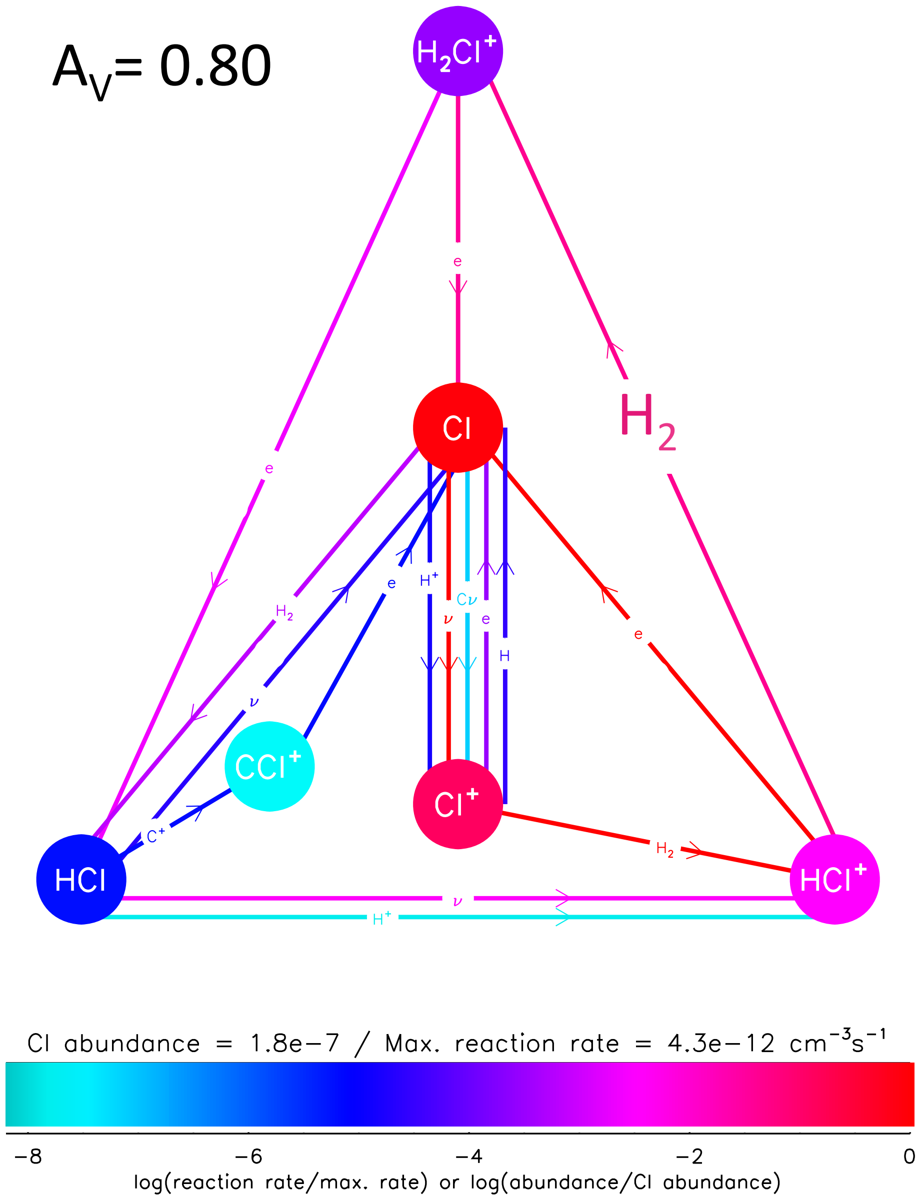
A_V= 0.00



Neufeld & Wolfire, ApJ (2009)

H_2Cl^+ chemistry

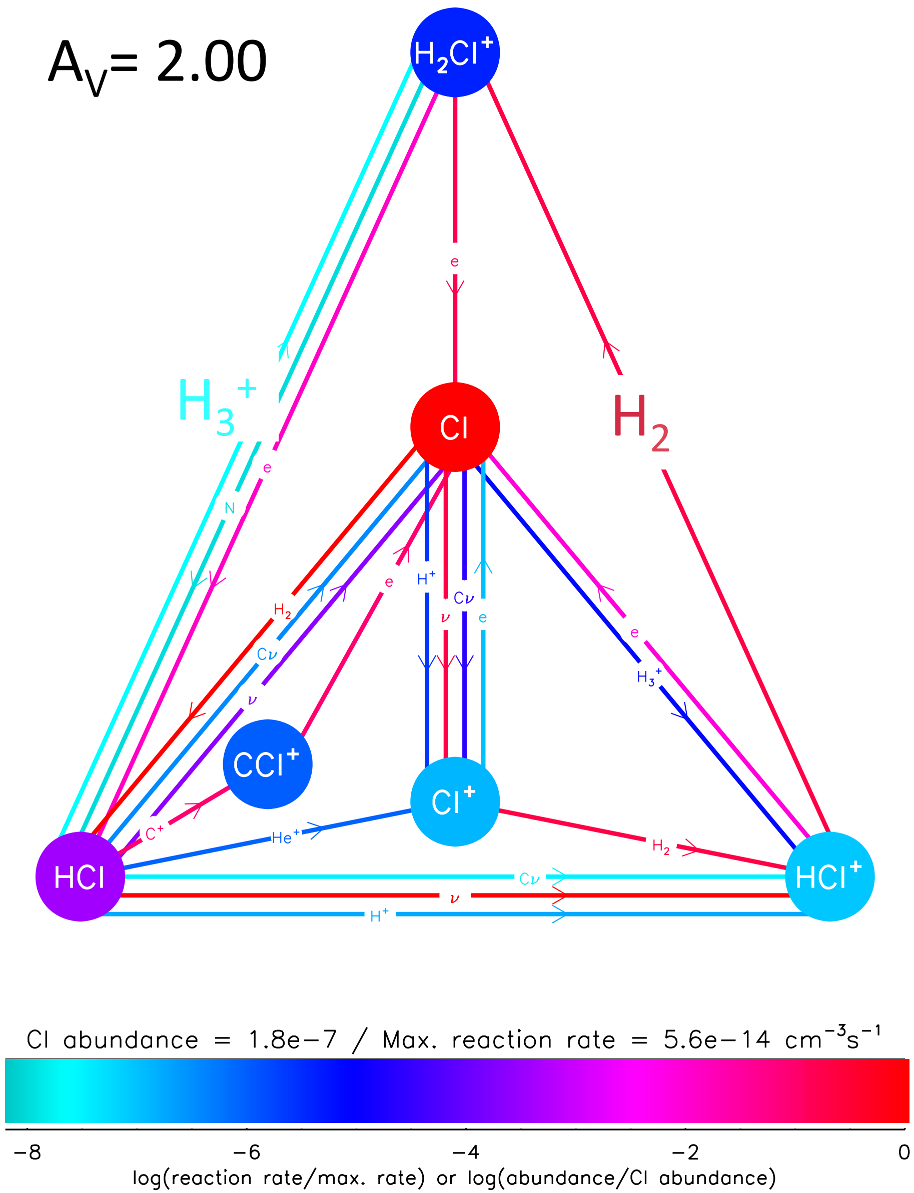
A_V= 0.80



Neufeld & Wolfire, ApJ (2009)

H_2Cl^+ chemistry

A_V= 2.00



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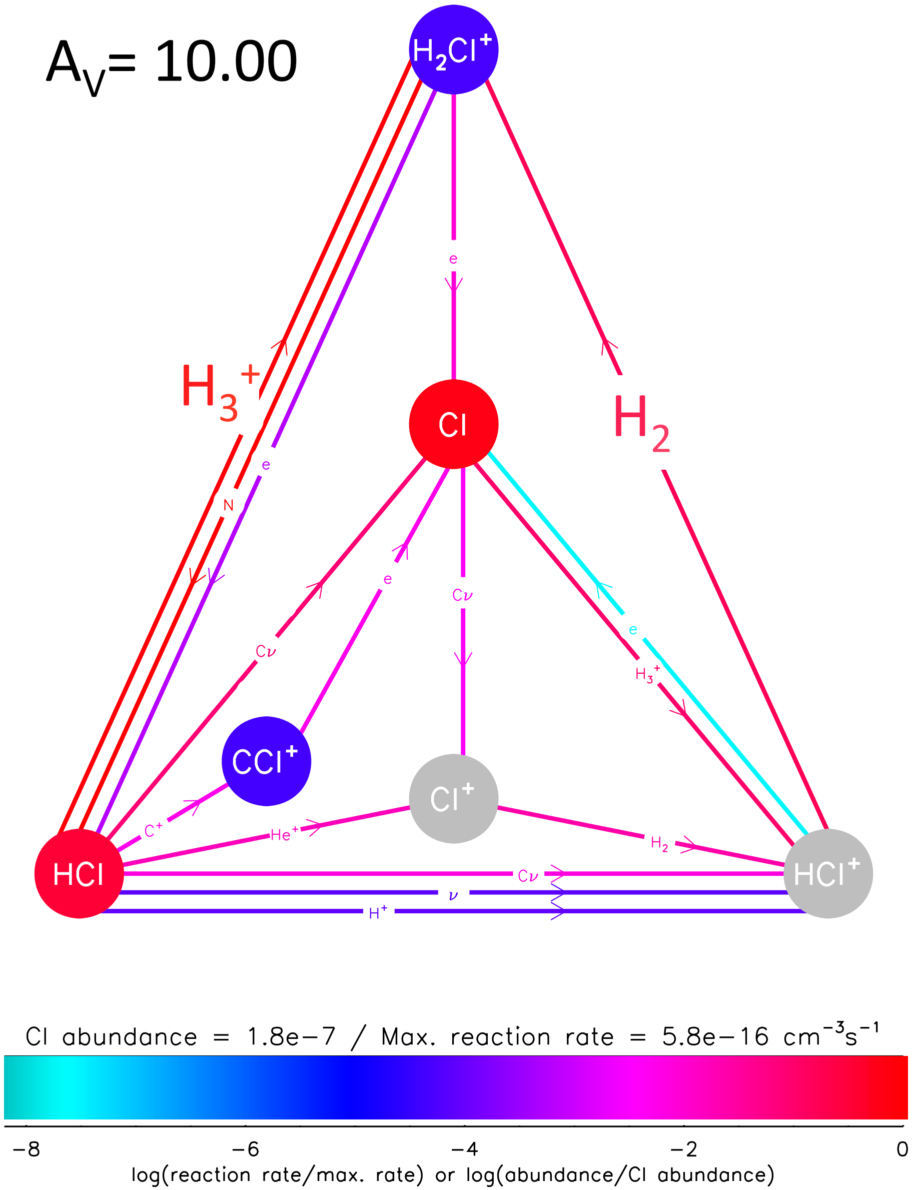
H_2Cl^+ chemistry



Neufeld & Wolfire, ApJ (2009)