Halogen-bearing interstellar molecules and what they can tell us

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Based on work with John Black, Maryvonne Gerin,
Javier Goicoechea, Paul Goldsmith, Cecile Gry,
Harshal Gupta, Eric Herbst, Nick Indriolo, Darek Lis,
Karl Menten, Raquel Monje, Bhaswati Mookerjea,
Carina Persson, Paule Sonnentrucker, and Mark Wolfire

New preprint posted last week on arXiv: 1505.00786

Halogen-bearing interstellar molecules detected to date

	HF	CF^+	HCl^+	H_2Cl^+	HCl
Discovery	1997*, 2010	2006	2012	2010	1985
Observatory	ISO*, Herschel	IRAM 30 m	Herschel	Herschel	CSO
Frequency (ground state)	1232 GHz	103 GHz	1444 GHz	485 GHz 782, 189 GHz	626 GHz
Minimum z for ALMA	0.30	0.00	0.52	0.00 (189 GHz) 0.09 (782 GHz)	0.00
	*Sgr B2 only				

Both F and Cl exhibit an distinctive thermochemistry

Element	**Dominant Ionization state in diffuse ISM**	$X^+ + H_2 \rightarrow XH^+ + H$	$X + H_2 \rightarrow XH + H$	$X + H_3^+ \rightarrow XH^+ + H_2$	**Driver**
C	C^+	$C^+ + H_2 \rightarrow CH^+ + H$	$C + H_2 \rightarrow CH + H$	$C + H_3^+ \rightarrow CH^+ + H_2$	Warm gas
S	S^+	$S^+ + H_2 \rightarrow SH^+ + H$	$S + H_2 \rightarrow SH + H$	$(S + H_3^+ \rightarrow SH^+ + H_2)$	Warm gas
O	O	$O^+ + H_2 \rightarrow OH^+ + H$	$O + H_2 \rightarrow OH + H$	$O + H_3^+ \rightarrow OH^+ + H_2$	Cosmic rays or warm gas
F	F	$(F^+ + H_2 \rightarrow HF^+ + H)$	$F + H_2 \rightarrow HF + H$	$(F + H_3^+ \rightarrow HF^+ + H_2)$	None
Cl	Cl^+	$Cl^+ + H_2 \rightarrow HCl^+ + H$	$Cl + H_2 \rightarrow HCl + H$	$Cl + H_3^+ \rightarrow HCl^+ + H_2$	UV
Ar	Ar	$Ar^+ + H_2 \rightarrow ArH^+ + H$	No reaction	$(Ar + H_3^+ \rightarrow ArH^+ + H_2)$	Cosmic rays

Blue : exothermic
Green: nearly exothermic
Red: endothermic
Parentheses: unimportant

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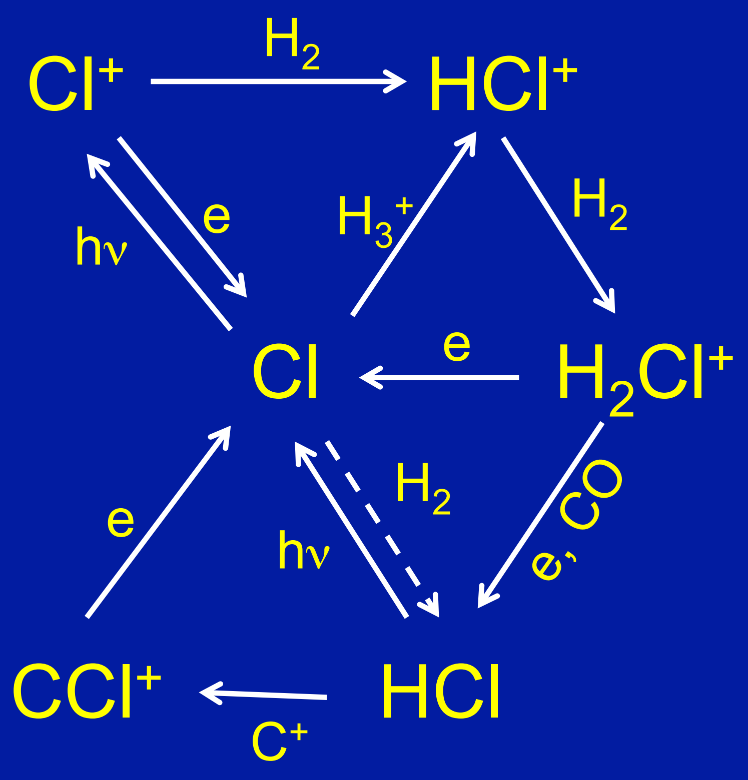
Chemistry of interstellar chlorine:

Chemistry of chlorine was investigated by:



Jura (1974)

Dalgarno et al. (1974)

Van Dishoeck & Black (1986)

Blake et al. (1986)

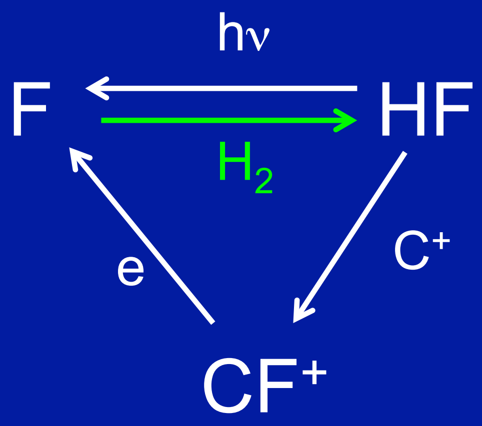
Schilke, Phillips & Wang (1995)

Federman et al. (1995)

Neufeld & Wolfire (2009)

Chemistry of interstellar fluorine

- Fluorine chemistry is very simple



$h\nu$

F

HF

H_2

e

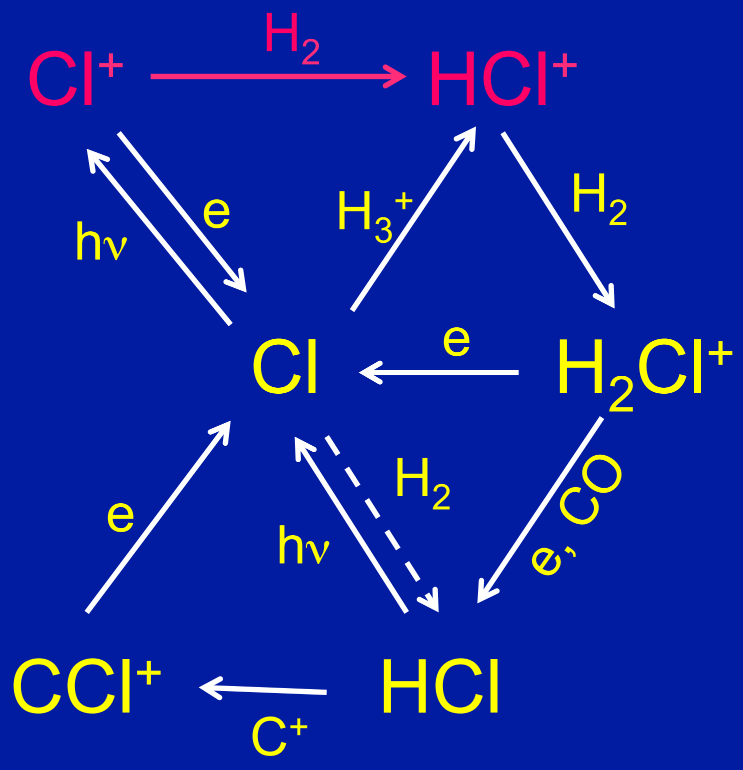
C^+

CF^+

(Neufeld et al. 2005, Neufeld & Wolfire 2009)

Chemistry of interstellar chlorine: diffuse clouds

- If H_2 is present, HCl^+ is produced rapidly
- But, HCl^+ is destroyed rapidly by reaction with H_2 to form H_2Cl^+
- H_2Cl^+ undergoes dissociative recombination to form Cl or HCl (with some branching ratio), HCl is photodissociated to form Cl
- Cl is only slowly ionized (I.P. ~ 12.97 eV) and becomes the dominant form of chlorine once H_2 becomes abundant.



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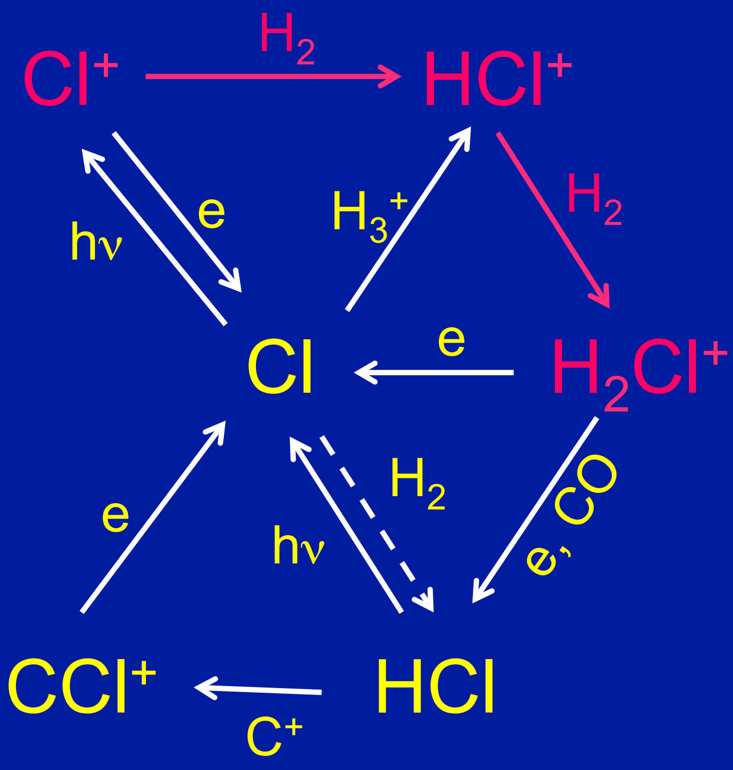

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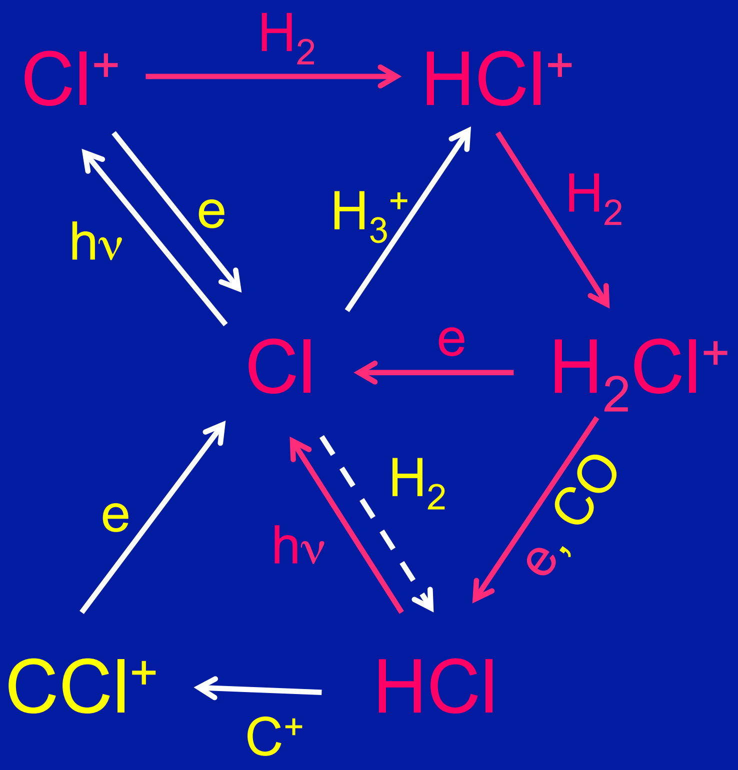

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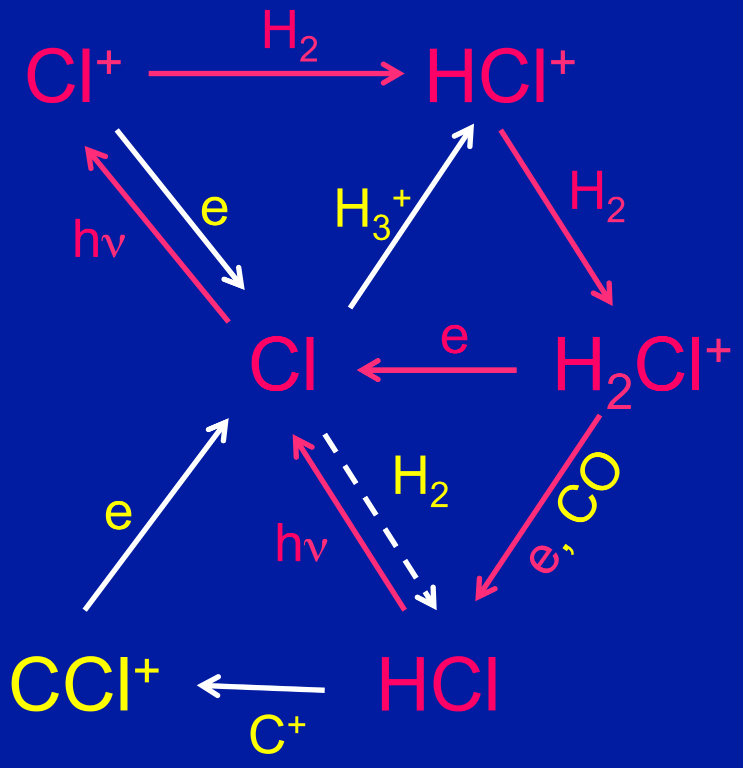

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Production	$F(H_2,H)HF$	$HF(C^+,H)CF^+$	$Cl^+(H_2,H)HCl^+$	$HCl^+(H_2,H)H_2Cl^+$	$H_2Cl^+(e,H)HCl$
Traces	Total H_2 column	Overlap of H_2 and C^+ (CO-dark H_2)	Gas with $f(H_2) \sim 0.02$	Gas with $f(H_2) \sim 0.2$	Gas with $f(H_2) \sim 1$
Extragalactic detections	Cloverleaf NGC 253 +			PKS 1830–211	
	*Sgr B2 only				

Emphasis of this talk

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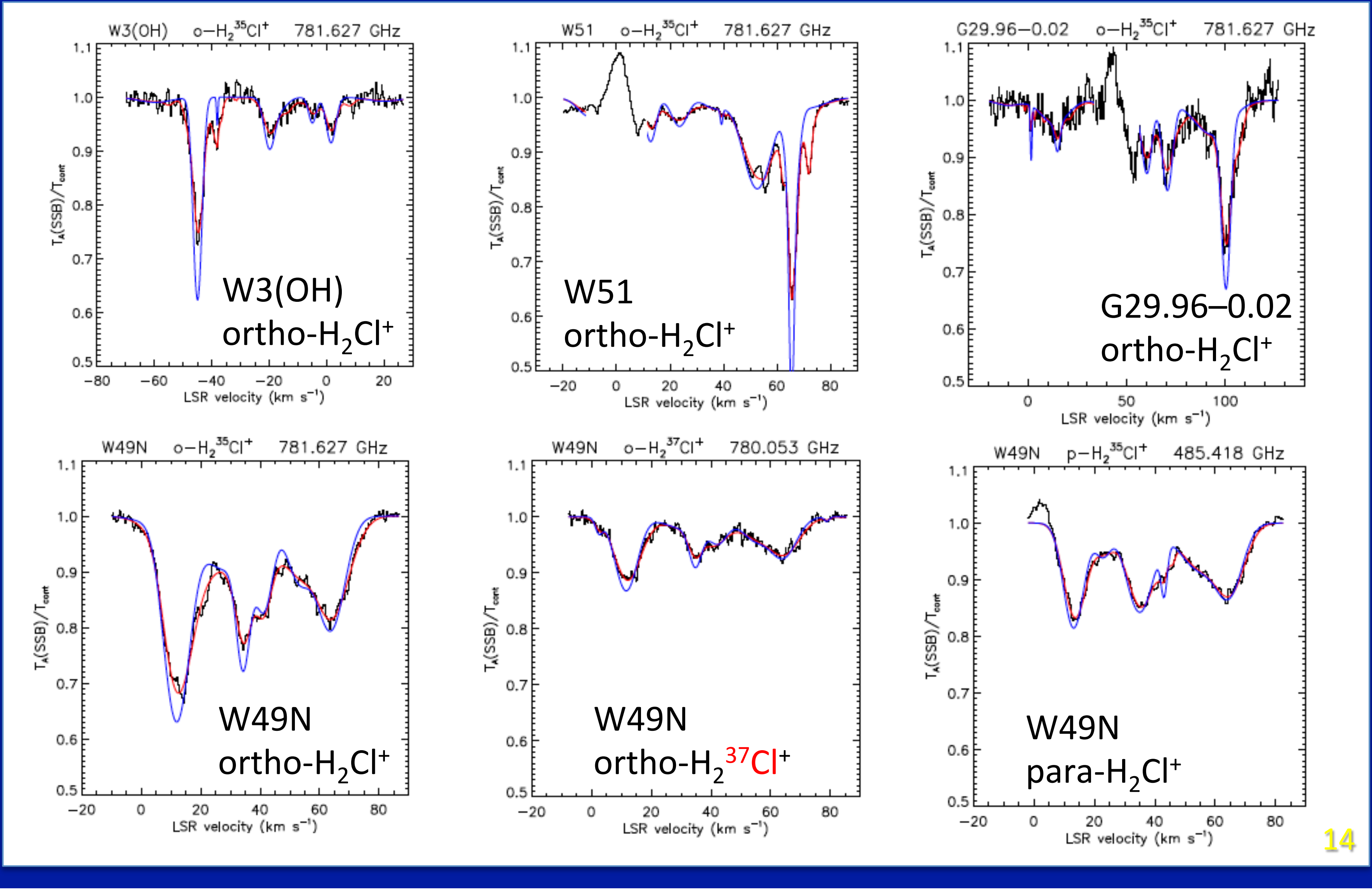
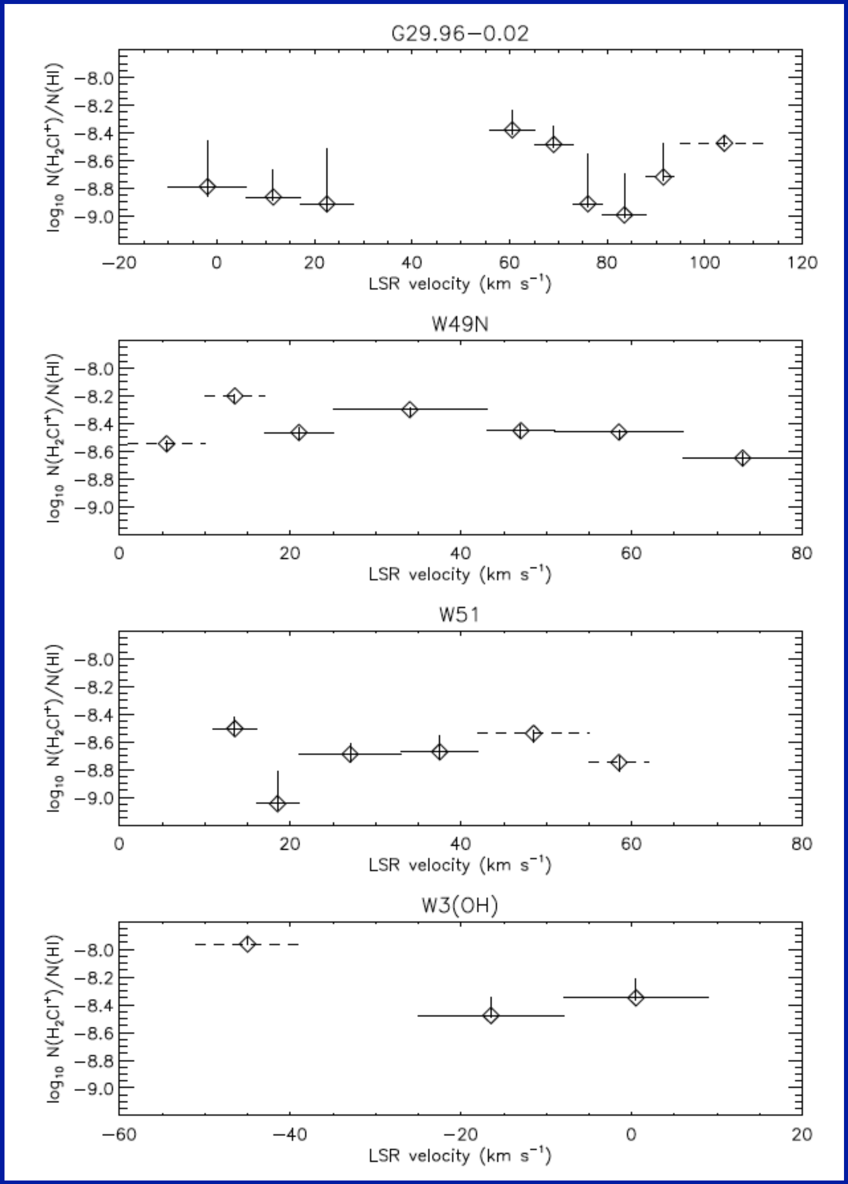
H_2Cl^+ detections, in absorption, toward four bright submillimeter sources (Neufeld et al. 2015)



H_2Cl^+ abundances are quite high



$N(H_2Cl^+)/N(H_0) = (0.9 – 4.8) \times 10^{-9}$

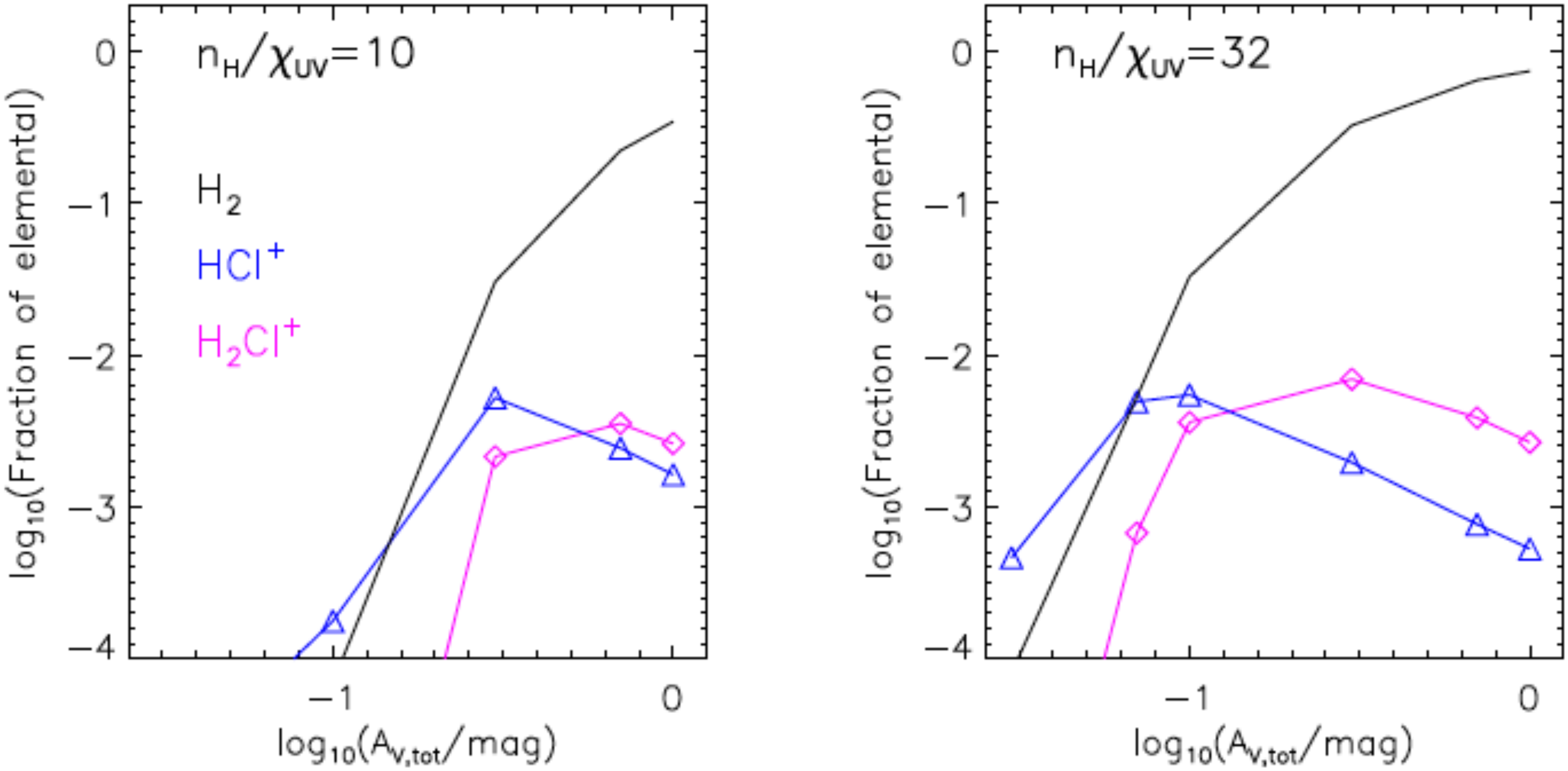
~ 1 – 5 % of gas-phase Cl

300 times as large as the fraction of O in H_2O^+, reflecting the fact that Cl^+ is the dominant ionization stage of Cl in diffuse atomic clouds

Actually up to a factor 5 larger than model predictions

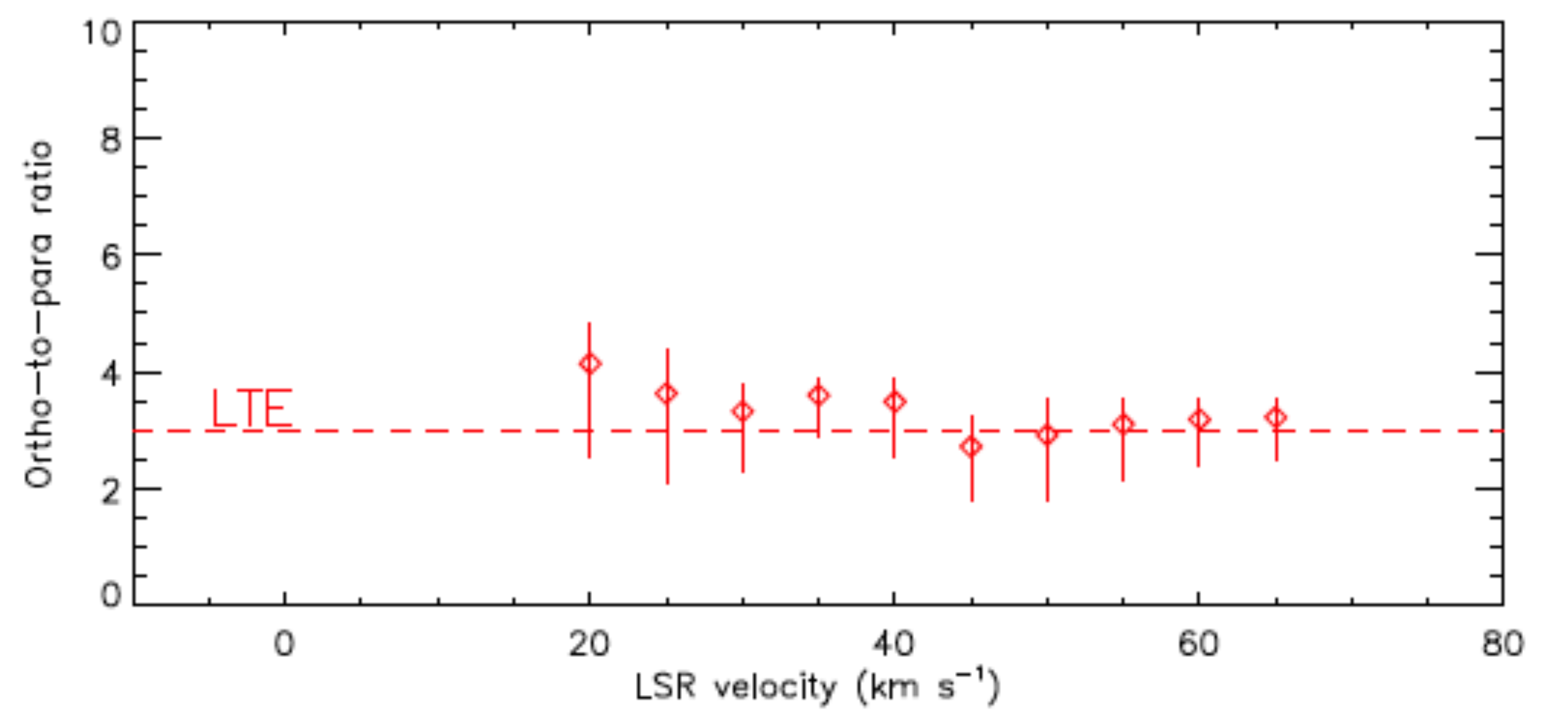
..an overestimated destruction mechanism (e.g. dissociative recombination)?

Model predictions



Neufeld et al. 2012, A&A

In W49N, we also have a secure detection of p-H_2Cl^+ (1_{11}-0_{00}): can measure the ortho/para ratio



Like other triatomic hydrides observed in the diffuse ISM (H_2O, H_2O^+), the OPR ~ 3 (the high-T LTE value , i.e. the ratio of statistical weights)

Interpretation of the OPR

H_2Cl^+ is initially formed with some ortho-to-para ratio, OPR_0

The forward and backwards reactions

$$\text{ortho-}H_2Cl^+ + H \leftarrow \rightarrow \text{para-}H_2Cl^+ + H$$

tend to drive it toward the ortho-to-para ratio corresponding to the gas temperature, OPR_{LTE}

Interpretation of the OPR

The actual ortho-to-para ratio lies somewhere between OPR_0 and OPR_{LTE}

$$OPR = x\ OPR_{LTE} + (1 - x)\ OPR_0$$

Exactly where it lies depends on the relative rates of o-p conversion and destruction

$$x = k_{op}/[k_{op}n(H) + k_{dr}n_e]$$

Two limits:

A) Rapid conversion: $x \sim 1 \Rightarrow OPR = OPR_{LTE}$

$(k_{op} >> 5 \times 10^{-11}\ cm^3\ s^{-1})$

B) Slow conversion: $x \sim 0 \Rightarrow OPR = OPR_0$

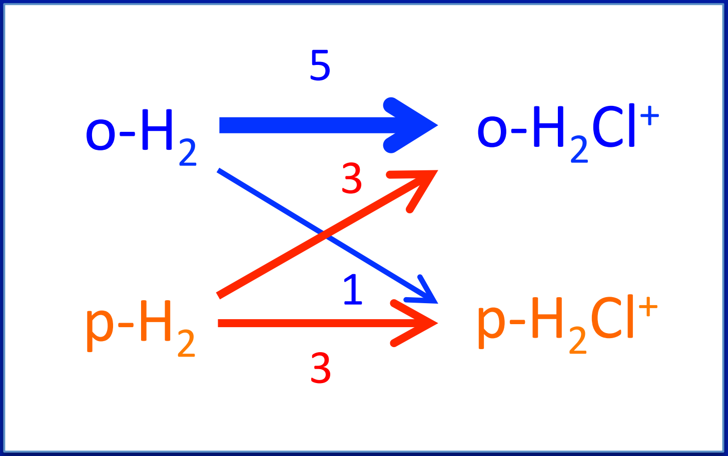
$(k_{op} << 5 \times 10^{-11}\ cm^3\ s^{-1})$

What is the formation OPR?

Two limits

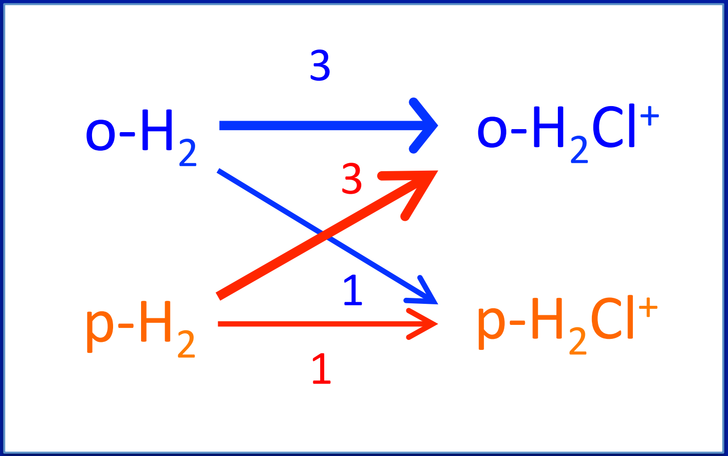
1) Complete spin scrambling:

$$OPR_0 = \frac{5\ OPR(H_2) + 3}{OPR(H_2) + 3}$$

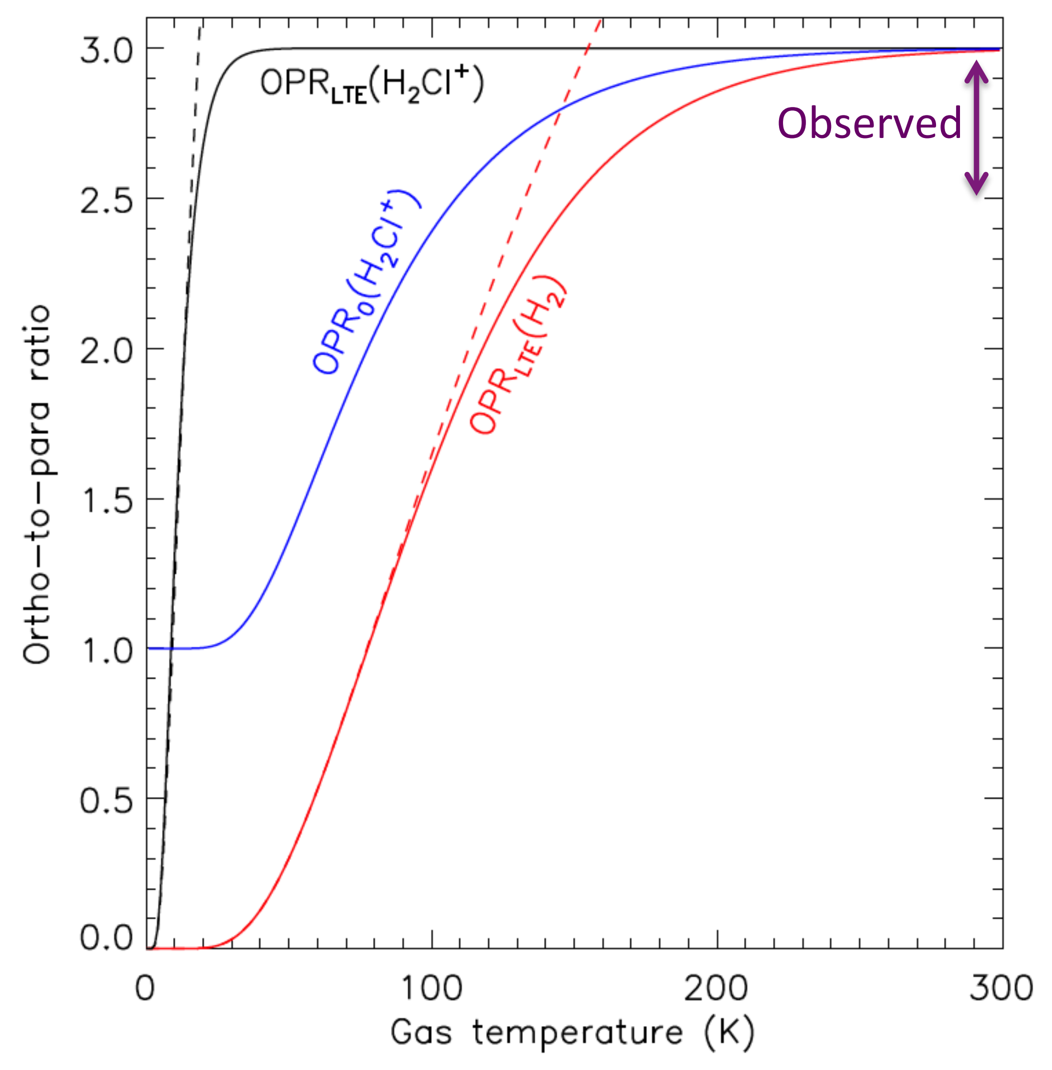


2) Hopping limit

$$OPR_0 = 3$$



Ortho-to-para ratios versus temperature



The observed OPR is typically consistent with 3 and greater than 2.5

A) Fast conversion: OPR = $\mathrm{OPR}_{\mathrm{LTE}}$

➔ $\mathrm{OPR}_{\mathrm{LTE}} > 2.6$ ➔ T > 20 K

B) Slow conversion: OPR = OPR_0

1) Complete scrambling

$\mathrm{OPR} = \mathrm{OPR}_0 = (5\ \mathrm{OPR}(\mathrm{H}_2) + 3)/(\mathrm{OPR}(\mathrm{H}_2) + 3)$

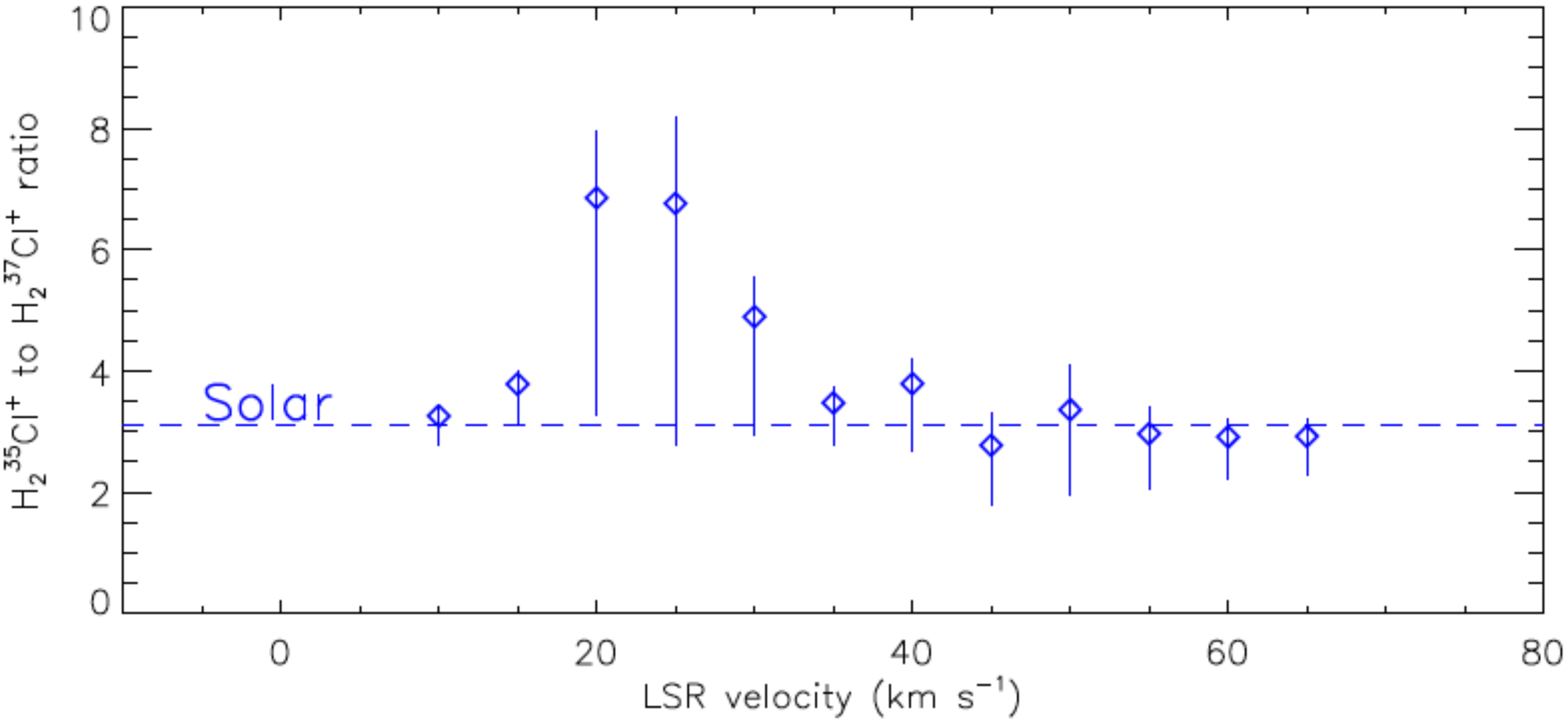
➔ $\mathrm{OPR}(\mathrm{H}_2) > 2$ ➔ T > 110 K

2) Hopping limit

$\mathrm{OPR} = \mathrm{OPR}_0 = 3$

➔ no constraint on physical conditions

$H_2{}^{35}Cl^+/H_2{}^{37}Cl^+$ ratio in W49N



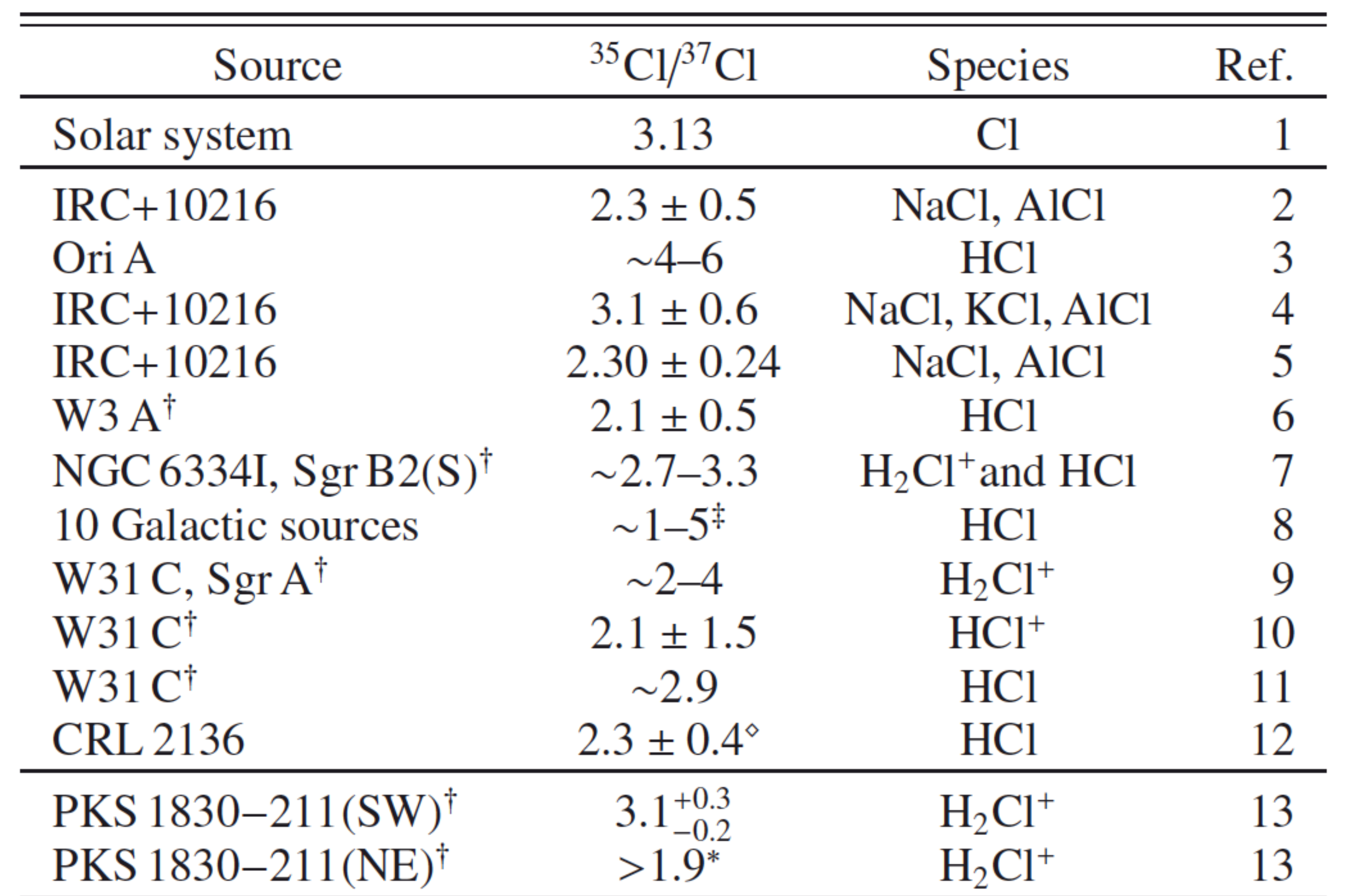
Observed ratio is consistent with solar system $^{35}Cl/^{37}Cl$ isotopic ratio of 3.1

Unique role of molecular observations in Galaxy and at high-z

Interpretation of the ^{35}Cl/^{37}Cl ratio

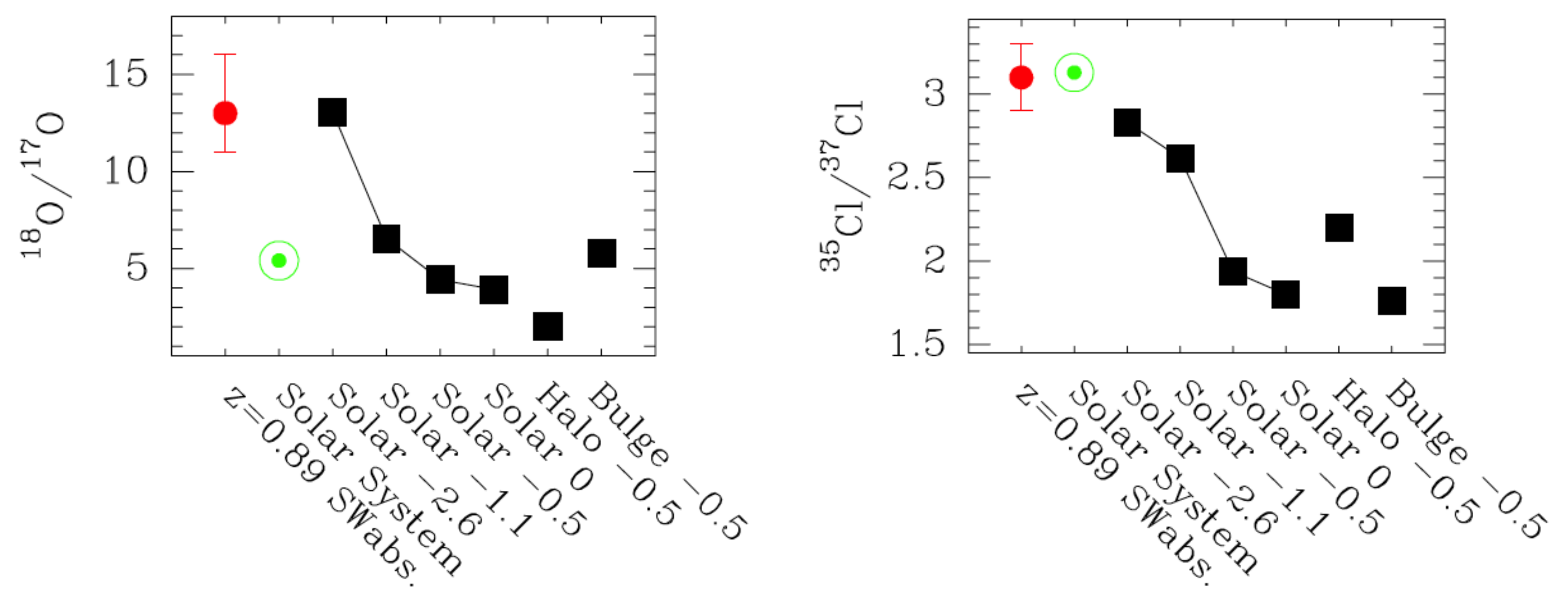
The ratio derived from $H_2{}^{35}Cl^+/H_2{}^{37}Cl^+$ is similar to that measured previously in a variety of environments

Muller et al. (2014)



Source	^{35}Cl/^{37}Cl	Species	Ref.
Solar system	3.13	Cl	1
IRC+10216	2.3 ± 0.5	NaCl, AlCl	2
Ori A	~4–6	HCl	3
IRC+10216	3.1 ± 0.6	NaCl, KCl, AlCl	4
IRC+10216	2.30 ± 0.24	NaCl, AlCl	5
W3 A†	2.1 ± 0.5	HCl	6
NGC 6334I, Sgr B2(S)†	~2.7–3.3	H_2Cl^+ and HCl	7
10 Galactic sources	~1–5‡	HCl	8
W31 C, Sgr A†	~2–4	H_2Cl^+	9
W31 C†	2.1 ± 1.5	HCl^+	10
W31 C†	~2.9	HCl	11
CRL 2136	2.3 ± 0.4°	HCl	12
PKS 1830–211 (SW)†	$3.1^{+0.3}_{-0.2}$	H_2Cl^+	13
PKS 1830–211 (NE)†	>1.9*	H_2Cl^+	13

This result is not exactly accounted for in current nucleosynthesis models



Kobayashi et al. (2011) results, as presented by Muller et al. (2014)

Summary of new results on H_2Cl^+

- Abundances $N(H_2Cl^+)/N(H^0) = 1 – 5 \times 10^{-9}$ lie a factor 1 – 5 above the maximum predictions for diffuse clouds → destruction rate overestimated?

- OPR ratios consistent with 3 → one or more of
  (1) T > 110 K (2) o/p conversion is fast and T > 20K
  (3) formation occurs without spin scrambling
  Need a better understanding of underlying chemistry

- $N(H_2{}^{35}Cl^+)/N(H_2{}^{37}Cl^+)$ consistent with solar system value of 3.1: not exactly accounted for by models