Physics, chemistry and excitation of hydride molecules

Introduction

Molecular and thermochemical properties

Some illustrations of the interplay between observations and chemical mechanisms

- New analysis of the $N^+ + H_2$ reaction and its isotopic variants
- Tracers of atomic gas: OH^+ / ArH^+
- Tracers of molecular gas : H_3^+, CH, HF

Examples of (photo)chemical excitation (OH, H_3O^+, NH_3)

Summary

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Laboratoire d'Étude du Rayonnement et de la Matière en Astrophysique et Atmosphères

Paris, December 12, 2016

The increasing attention to hydrides

After the first detection of CH^+, CH in absorption against bright stars ….

decreasing frequency

UV/Visible absorption spectroscopy : H_2, HD, OH, OH^+, NH

Vibrational IR absorption spectra : H_3^+, CH_4

Rotational submillimeter spectra:

ISO: CH^+, CH_2 , H_2O

Herschel: CH, CH^+, OH, H_2O, OH^+, H_2O^+, H_3O^+, NH, NH_2, NH_3, SH, SH^+, H_2S, HF, HCl, HCl^+, H_2Cl^+, ArH^+

Inversion spectra: NH_3, H_3O^+

Λ doubling: OH, CH

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Rotational submillimeter spectra

very luminous region of massive star formation can be used as a background THz source

Absorption by gas in foreground material

"clean experiment" allowing robust determination of molecular column densities.

Inversion spectra: NH_3, H_3O^+

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Importance of electronic structure

- ✓ Spectroscopy
  - UV/visible electronic transitions (talk of S. Federman)
  - rotational/vibrational spectra pattern highly dependent on the ground electronic state property (talk of Domenech)
  - intensity pattern / opacities (talk of Tennyson)
- ✓ Collisional excitation
  - PES computations
  - Collision equations and possible approximations for the different angular momenta (talks of Faure, Lique)
- ✓ Chemical reactivity
  - open shell radicals are more reactive than closed electronic shells. (talks of Schneider, Alcaraz)

Closed shell hydrides

diatomic		triatomics		4	5	6
$X\ ^1\Sigma^+_g$ $D_{\infty h}$	$X\ ^1\Sigma^+$ $C_{\infty v}$	$X\ ^1A'_1$ C_{3v}	$X\ ^1A_1$ C_{2v}	$X\ ^1A_1$ C_{3v}	$X\ ^1A_1$ T_d	
H_2		H_3^+	H_2O	NH_3	CH_4	
	HF		H_2S	H_3O^+		
	HCl		H_2Cl^+			
	CH^+					
	ArH^+					

detected in galactic and/or extragalactic ISM

Closed shell hydrides

diatomic		triatomics		4	5	6
$X\ ^1\Sigma^+_g$ $D_{\infty h}$	$X\ ^1\Sigma^+$ $C_{\infty v}$	$X\ ^1A'_1$ C_{3v}	$X\ ^1A_1$ C_{2v}	$X\ ^1A_1$ C_{3v}	$X\ ^1A_1$ T_d	X e-C_S under study
H_2	LiH	H_3^+	H_2O	NH_3	CH_4	CH_5^+
	HF		H_2S	H_3O^+		
	HCl		H_2Cl^+	CH_3^+		
	BH		H_2F^+			
	CH^+					
	ArH^+					
	HeH^+					
	SiH^+					

additional interesting candidates

Hydrides with non zero spin

diatomic			triatomic				4
$X\ ^2\Sigma^+$ $C_{\infty v}$	$X\ ^2\Pi$ $C_{\infty v}$	$X\ ^3\Sigma^-$ $C_{\infty v}$	$X\ ^2A_1$ C_{2v}	$X\ ^2B_1$ C_{2v}	$X\ ^2B_2$ C_{2v}	$X\ ^3B_1$ C_{2v}	$X\ ^2A_2$ D_{3h}
	CH	NH		NH_2	H_2O^+	CH_2	CH_3
	OH	OH^+					
	SH	SH^+					
	HCl^+						

detected in the ISM

Hydrides with non zero spin

diatomic			triatomic				4
$X\ ^2\Sigma^+$ $C_{\infty v}$	$X\ ^2\Pi$ $C_{\infty v}$	$X\ ^3\Sigma^-$ $C_{\infty v}$	$X\ ^2A_1$ C_{2v}	$X\ ^2B_1$ C_{2v}	$X\ ^2B_2$ C_{2v}	$X\ ^3B_1$ C_{2v}	$X\ ^2A_2$ D_{3h}
H_2^+	CH	NH	BH_2	NH_2	H_2O^+	CH_2	CH_3
LiH^+	OH	OH^+	CH_2^+			NH_2^+	NH_3^+
BeH	SH	SH^+					
MgH	HCl^+						
CaH	NH^+						

additional interesting candidates

+ FeH : $X^4\Delta$

Isotopically substituted ISM hydrides

diatomics			3	4	5
X $^1\Sigma^+$	X $^2\Pi$	X $^3\Sigma^-$	X $^1A_1$	X $^1A_1$	X $^1A_1$
HD	OD	ND	H_2D^+	NH_2D	*CH_3D**
$^{13}CH^+$			D_2H^+	ND_2H	NH_3D^+
$^{38}ArH^+$			HDO	ND_3	
			D_2O	$^{15}NH_3$	
				$^{15}NH_2D$	
				*CH_2D^+**	

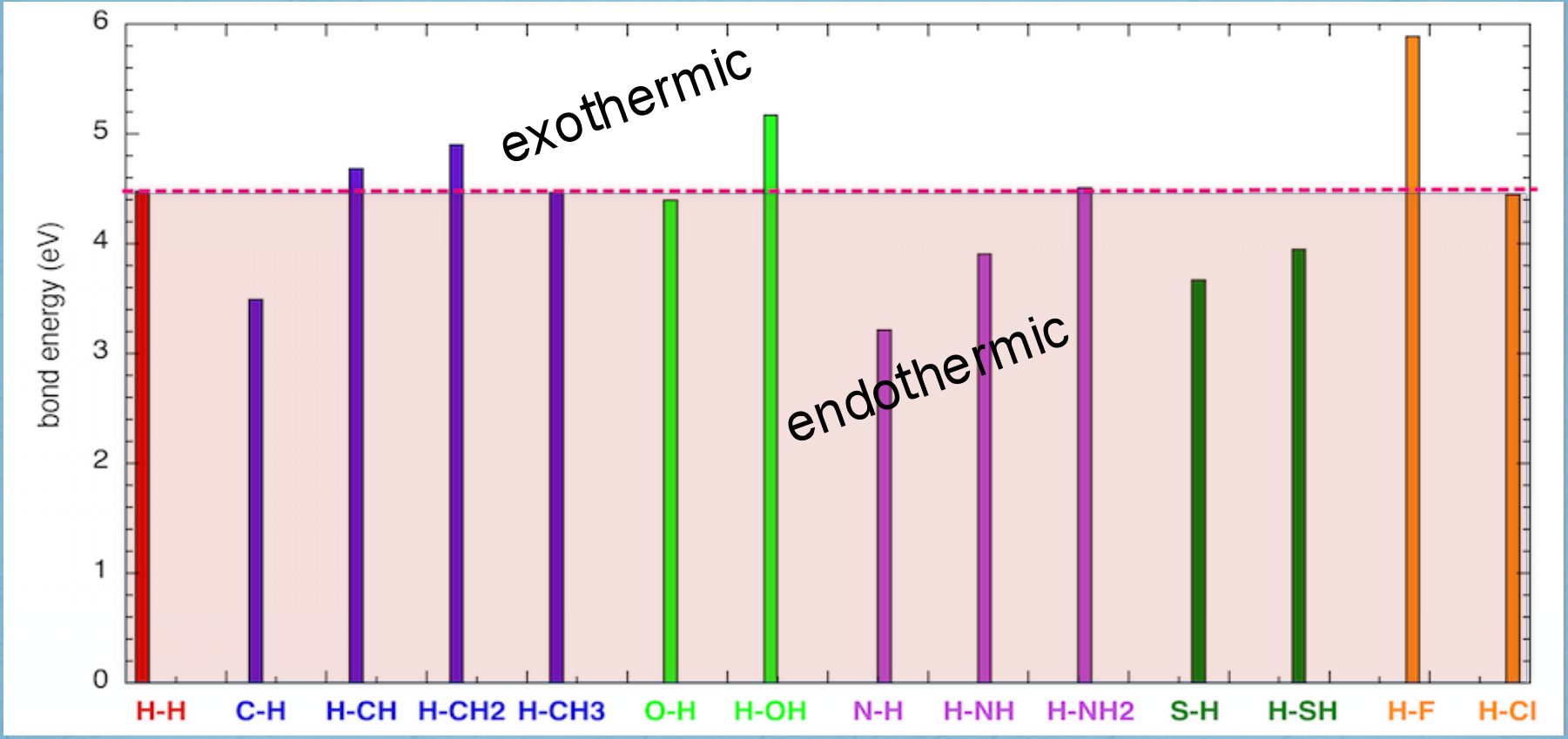
* *tentative*

See talk of P. Caselli

Thermodynamical properties (1)

$X + H_2 \rightarrow XH + H$

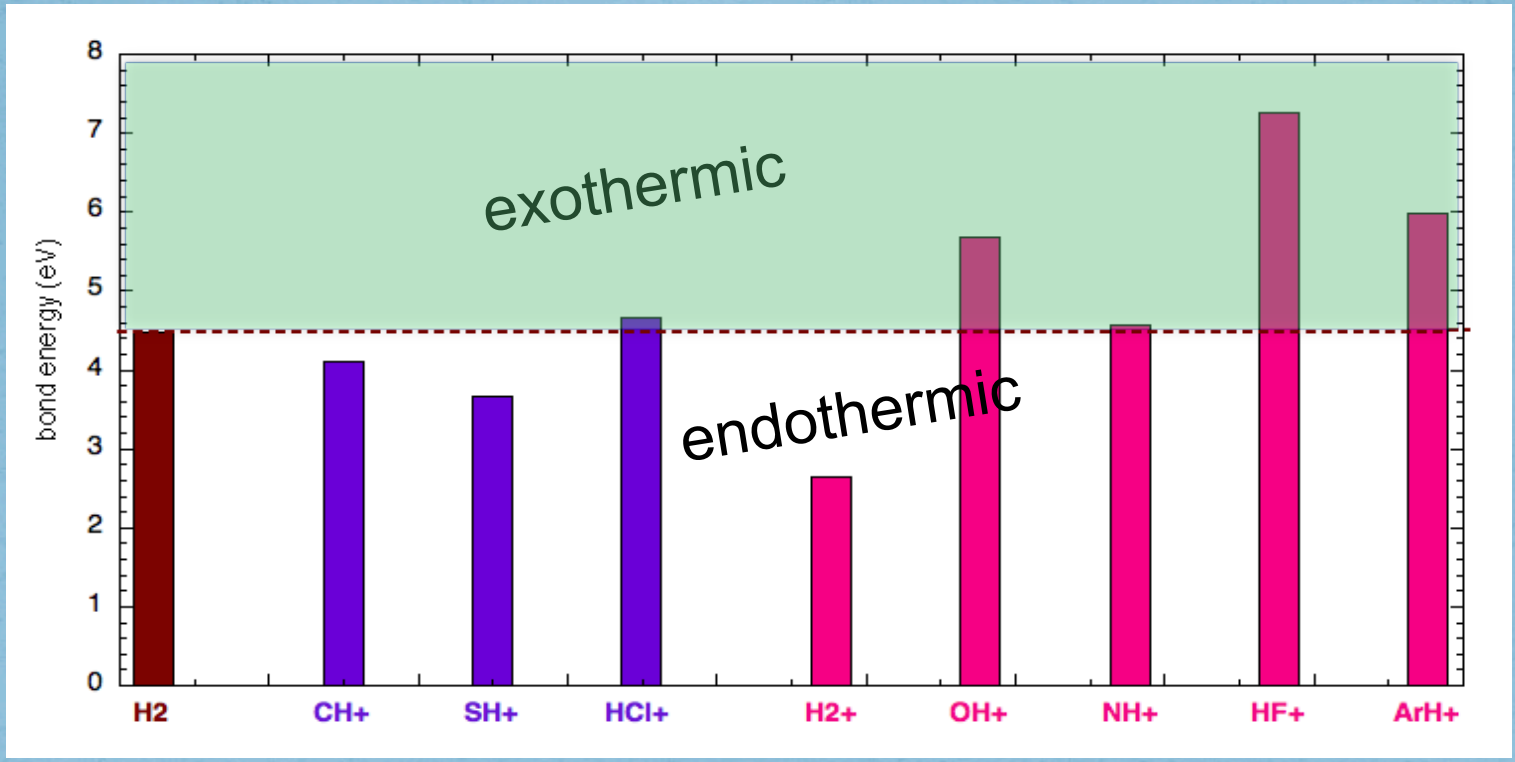
possibility of activation barriers



carbon oxygen nitrogen sulfur halogen

Thermodynamical properties (2)

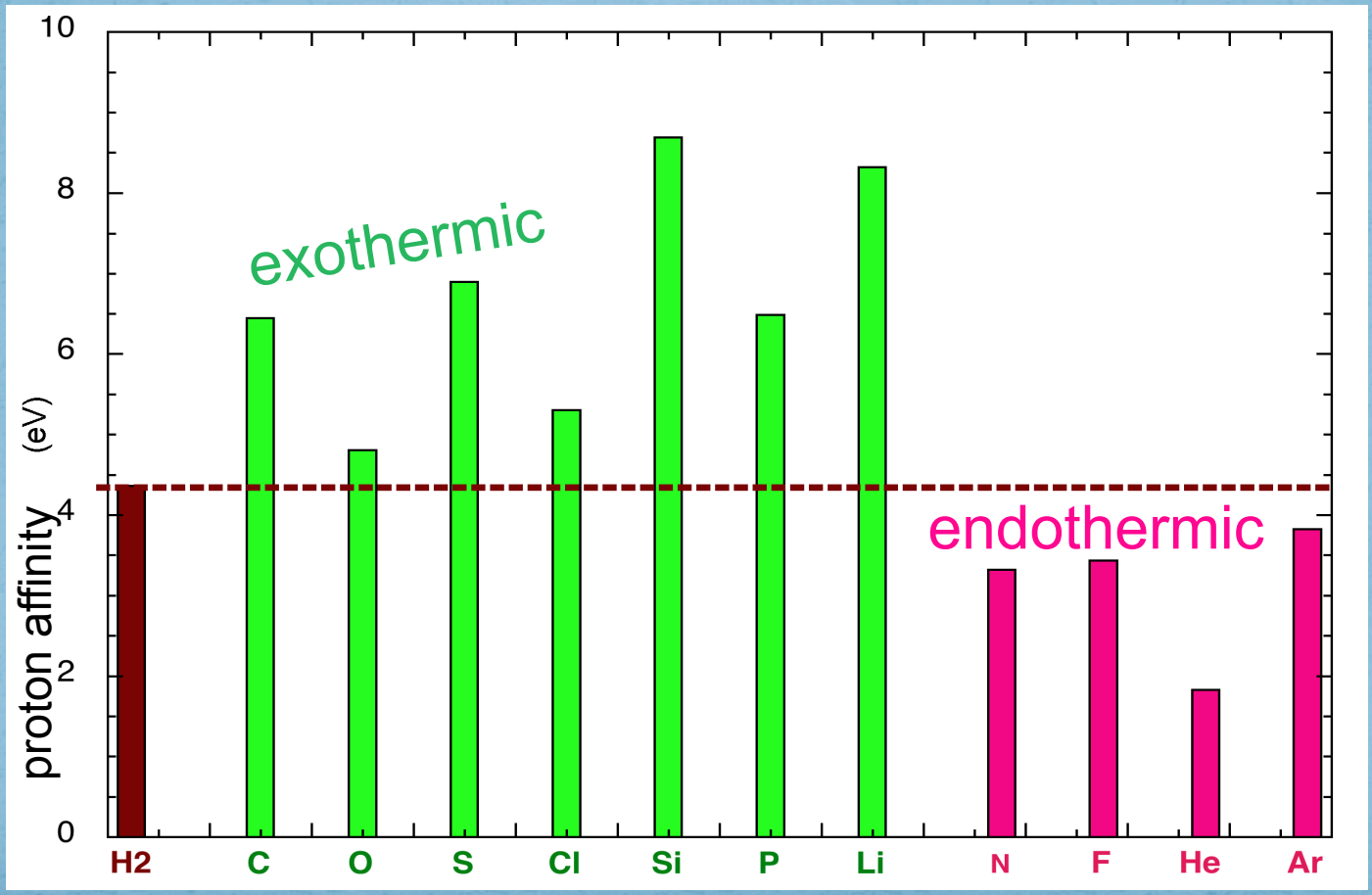
$$X^+ + H_2 \rightarrow XH^+ + H$$



Ionization source: photons cosmic rays

Thermodynamical properties (3)

$$X + H_3^+ \rightarrow XH^+ + H_2$$



Chemical gas phase scenarii

Element	Ionization potential (eV)	Endothermicity (Kelvin equivalent = $\Delta E/k_B$) for $X + H_2 \rightarrow XH + H$	Endothermicity (Kelvin equivalent = $\Delta E/k_B$) for $X^+ + H_2 \rightarrow XH^+ + H$	Endothermicity (Kelvin equivalent = $\Delta E/k_B$) for $X + H_3^+ \rightarrow XH^+ + H_2$	comments
He	24.587	No reaction	Exothermic, but primary channel is to He + H + H^+	29,000	unstable ground state of HeH
C	11.260	11,000	4,300 ☑		energy input required w C^+
N	14.534	15,000	??	10,000	state to state chemistry (o/p)
O	13.618	920 ☑	☑	☑	CRs / warm neutral chemistry
F	17.423	☑		10,000	neutral chemistry
Ne	21.564	No reaction	Exothermic, but primary channel is to Ne + H + H^+	27,000	Poorly known NeH^+ spectro
Si	8.152	17,000	15,000		energy input required w Si^+
P	10.487	19,000	13,000		energy input required w P^+
S	10.360	10,000	10,000 ☑		energy input required w S^+
Cl	12.968	515	☑		sensitivity to threshold photons
Ar	15.760	No reaction	☑	6,400	Cosmic rays / small f_{H2}

Exothermic reaction of element in its main ionization state

Endothermic reaction of element in its main ionization state

Exothermic reaction of element **not** in main ionization state

Endothermic reaction of element **not** in main ionization state

☑ Important formation pathway

adapted from Gerin et al. 2016, ARAA 54, 181 and Neufeld 2016, SOFIA conference

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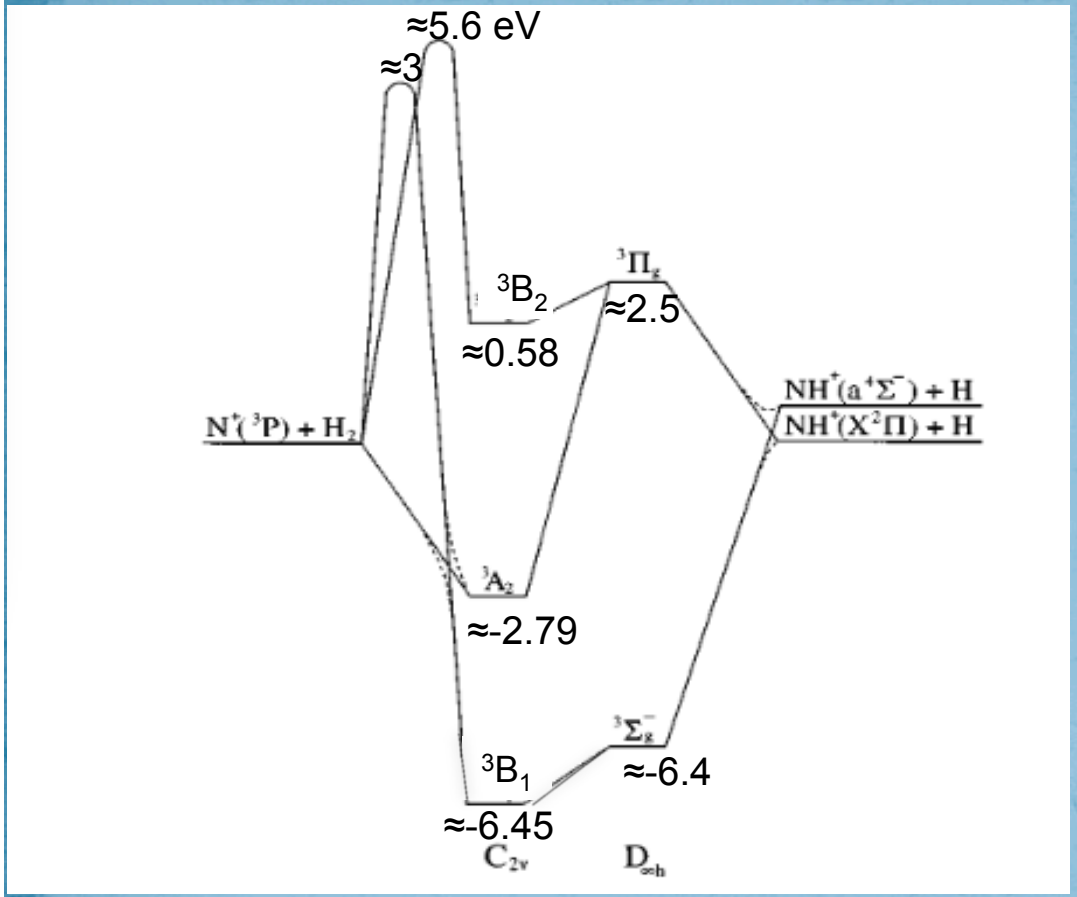
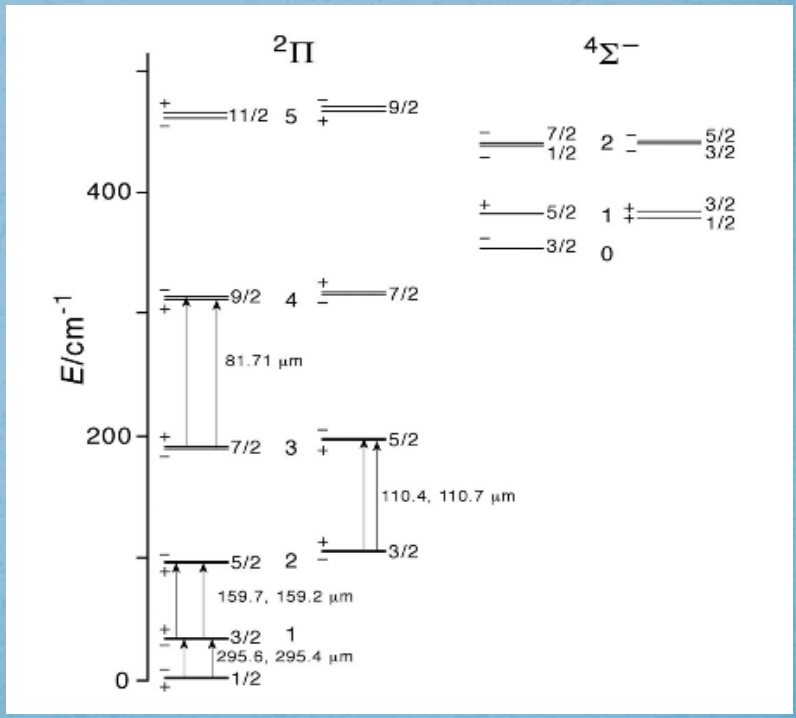


Electronic states correlation diagram for C_{2V} and $D_{\infty h}$ symmetries
Gonzalez et al. 1986, Chem.Phys. 104, 57
Russel & Manolopoulos 1999, JCP110, 177

Almost thermo-neutral reaction

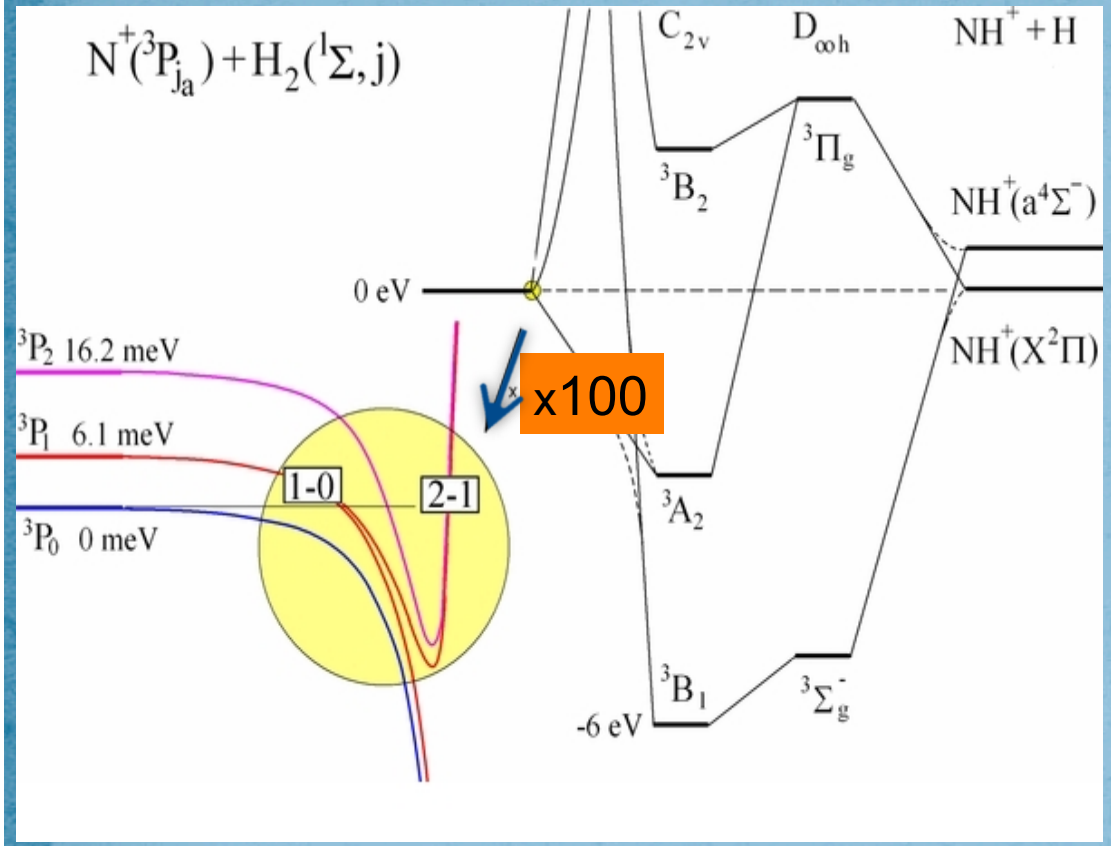
Fine structure channels mixed to reactive channels

Highly perturbed structure of NH^+



Hubers et al. 2009, JCP131, 4311

Revisiting the $N^+ (^3P_j) + H_2 (J) \rightarrow NH^+ + H$ reaction (1)

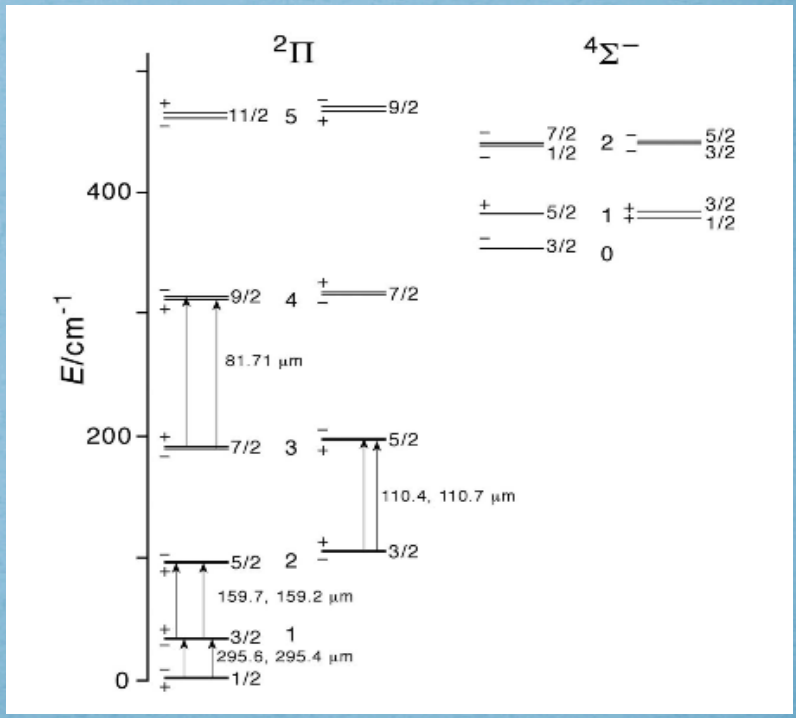


Electronic states correlation diagram for C_{2V} and $D_{\infty h}$ symmetries including fine structure of N^+
Zymak et al. 2013, ApJ 768, 86

Almost thermo-neutral reaction

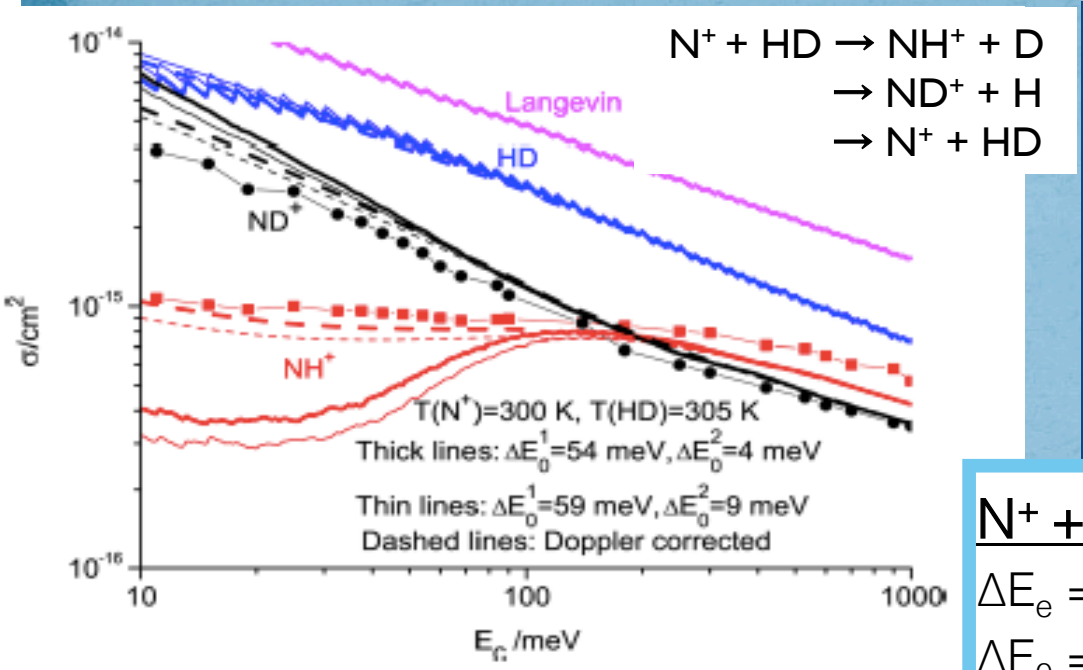
Fine structure channels mixed to reactive channels

Highly perturbed structure of NH^+



Hubers et al. 2009, JCP131, 4311

Revisiting the $N^+ (^3P_j) + H_2 (J) \rightarrow NH^+ + H$ reaction (2)



Use of statistical theory of reactive collisions where the energies of the fine structure states (j=0, 1, 2) of the N^+ ions are treated on an equal footing with other energies of internal rotation motions.

Critical parameter : ΔE_e : equilibrium ergicity (vibrationless energy variation)

Grozdanov & McCarroll 2015, JPCA119, 5988

interprete the collision cross sections measurements of Sunderlin & Armentrout 1994, JCP 100, 5639 of the $N^+ + H_2$ (HD, D_2) reactions

$$101 \leq \Delta E_e \leq 106 \text{ meV}$$

$N^+ + H_2$

$$\Delta E_e = D_e(H_2) - D_e(NH^+) = \Delta E_0 + E_{00}(H_2) - E_{00}(NH^+)$$

$$\Delta E_0 = D_0(H_2) - D_0(NH^+)$$

$N^+ + HD$

NH^+ channel

$$\Delta E_e = D_e(HD) - D_e(NH^+) = \Delta E_0^1 + E_{00}(HD) - E_{00}(NH^+)$$

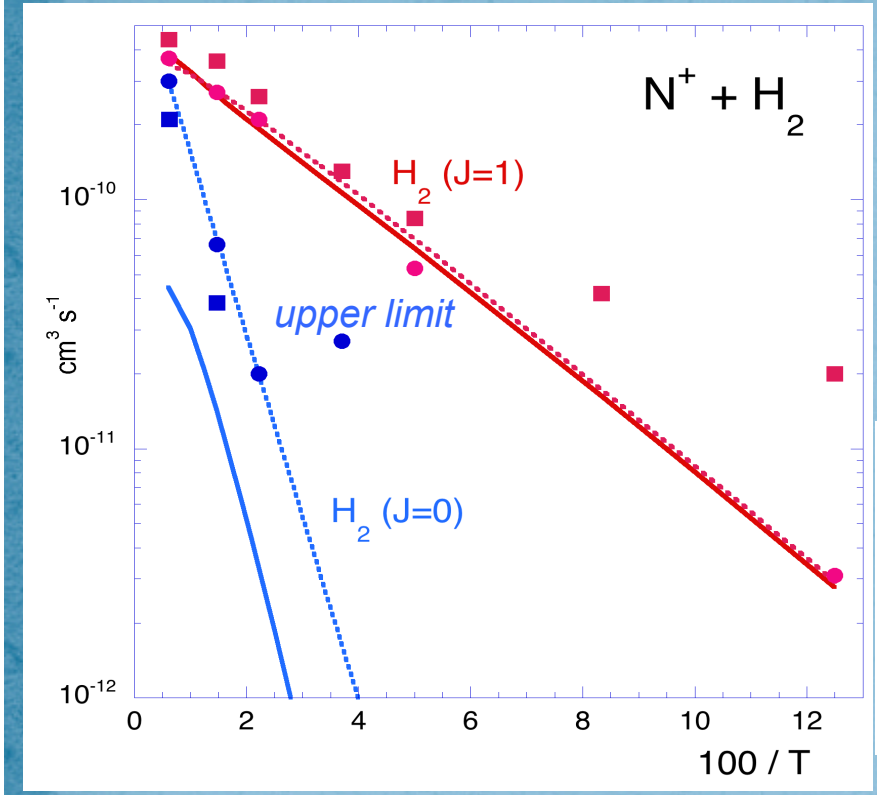
$$\Delta E_0^1 = D_0(HD) - D_0(NH^+)$$

ND^+ channel

$$\Delta E_e = D_e(HD) - D_e(ND^+) = \Delta E_0^2 + E_{00}(HD) - E_{00}(ND^+)$$

$$\Delta E_0^2 = D_0(HD) - D_0(ND^+)$$

Revisiting the $N^+ (^3P_j) + H_2 (J) \rightarrow NH^+ + H$ reaction (3)



Constraining the critical parameter ΔE_e by comparison with low temperature measurements of reaction rate constants

ΔE_e = 101 meV

● ● experimental results of Marquette et al. 1988, JCP 89

■ ■ experimental results of Zymak et al. 2013, ApJ 768, 86

——: new statistical model with best choice of ΔEe (Grozdanov et al 2016, A&A 589, A105)

: Dislaire et al. 2012, A&A 537, A20 fits of Marquette et al. experiment (JCP89, 2041)

- Experimental results of o-H_2 from Marquette et al. reproduced satisfactorily.
- p-H_2 less satisfactory
- state to state reaction rates including fine structure states of N^+ and H_2 (J=0,1)

Endothermicities computed with the assumption that ΔE_e = 101 meV.

Reaction			ΔE_0 (meV)	ΔE_0 (K)
$N^+ (^3P_0) + H_2 (J = 0)$	→	$NH^+ + H$	18.53	215.0
$N^+ (^3P_0) + H_2 (J = 1)$	→	$NH^+ + H$	3.84	44.6
$N^+ (^3P_1) + H_2 (J = 0)$	→	$NH^+ + H$	12.49	144.9
$N^+ (^3P_1) + H_2 (J = 1)$	→	$NH^+ + H$	-2.20	
$N^+ (^3P_2) + H_2 (J = 0)$	→	$NH^+ + H$	2.31	26.8
$N^+ (^3P_2) + H_2 (J = 1)$	→	$NH^+ + H$	-12.38	
$N^+ (^3P_0) + HD (J = 0)$	→	$ND^+ + H$	4.21	48.9
$N^+ (^3P_0) + HD (J = 0)$	→	$NH^+ + D$	54.06	627.3
$N^+ (^3P_1) + HD (J = 0)$	→	$ND^+ + H$	-1.83	
$N^+ (^3P_1) + HD (J = 0)$	→	$NH^+ + D$	48.02	5
$^{15}N^+ (^3P_0) + H_2 (J = 0)$	→	$NH^+ + H$	18.2	
$^{15}N^+ (^3P_0) + H_2 (J = 1)$	→	$NH^+ + H$	3.51	
$^{15}N^+ (^3P_0) + HD (J = 0)$	→	$^{15}ND^+ + H$	3.74	

The measured reaction rate coefficient of N^+ + HD is larger than that of N^+ + o-H_2 despite a larger endothermicity!

Reaction rate coefficients of Marquette et al. 1988, JCP 89, 20411

Reaction		8 K	20 K	27 K	45 K	68 K	163 K
$N^+ + nH_2$	(1)	2.3(−12)	4.0(−11)	1.0(−10)	1.6(−10)	2.2(−10)	3.5(−10)
$N^+ + pH_2$	(6)	···	*<1(−12)*	*2.7(−11)*	2.0(−11)	6.6(−11)	3.0(−10)
	(2)	···	···	···	3.3(−12)	1.0(−11)	7.4(−11)
$N^+ + HD$	(4)	···	1.4(−10)	···	···	···	···

$$k(n - H_2) \sim \frac{3}{4}\, k(o - H_2)$$ at 20K

$k(o\text{-}H_2) \approx 5.3\ 10^{-11}\ cm^3\ s^{-1}$ at 20K

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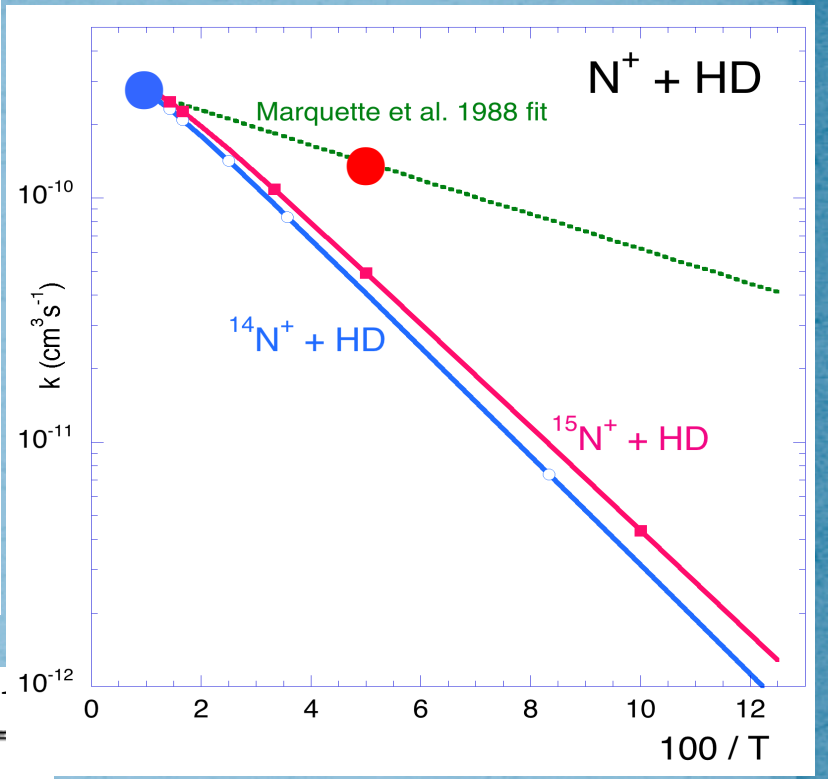
$N^+ (^3P_1) + HD (J = 0)$	→	$NH^+ + D$	48.02	557.2
$^{15}N^+ (^3P_0) + H_2 (J = 0)$	→	$NH^+ + H$	18.2	211.2
$^{15}N^+ (^3P_0) + H_2 (J = 1)$	→	$NH^+ + H$	3.51	40.7
$^{15}N^+ (^3P_0) + HD (J = 0)$	→	$^{15}ND^+ + H$	3.74	43.4



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$$k(n - H_2) \sim \frac{3}{4}\, k(o - H_2)$$

$k(o\text{-}H_2) \approx 5.3\ 10^{-11}\ cm^3\ s^{-1}$

Grozdanov et al. 2016, A&A589, A105

Theoretical statistical model calculations based on computed endothermicities

State to state reaction rate coefficients for $N^+(J) + H_2(J)$, HD(J) and $^{15}N^+(J) + H_2(J)$, HD(J).

Endothermicities computed with the assumption that ΔE_e = 101 meV.

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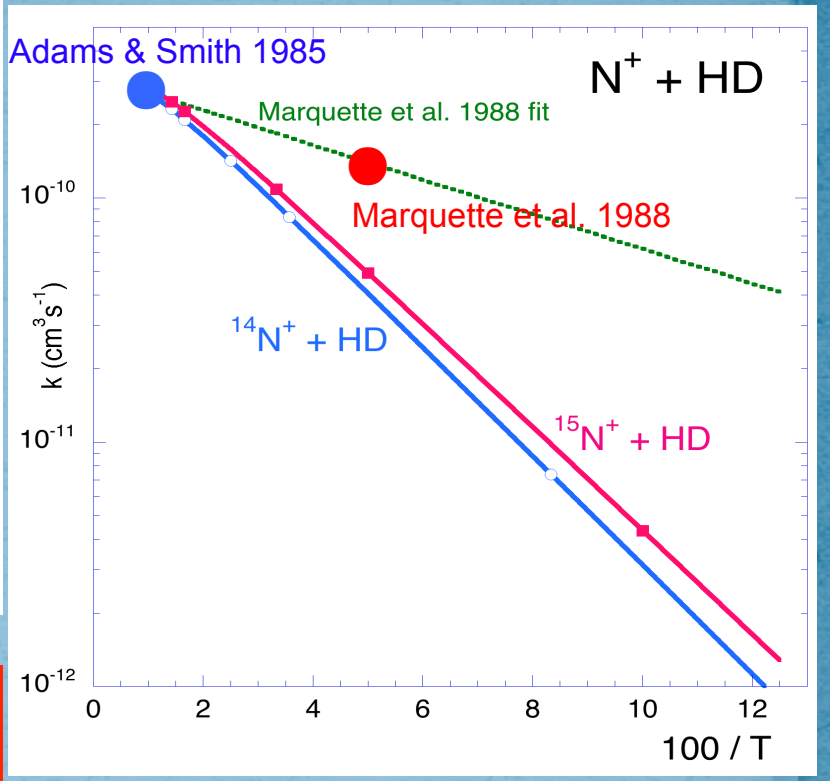

The quite large value reported for N^+ + HD rate coefficient is somewhat puzzling

The proposed fit of Marquette et al,

k=3.17 10^{-10} exp(-16.3/T), is based on this *single* point and the measurement of Adams & Smith 1985, CPL117, 67 at 300K.

Grozdanov et al. 2016, A&A589, A105

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Revisiting the $N^+ (^3P_j) + H_2$ (J) → $NH^+ + H$ reaction (4)

Suggested fits for the various isotopics variants (Grozdanov et al, 2016)

Reaction			k ($cm^3\ s^{-1}$)
$N^+ + p-H_2$	→	$NH^+ + H$	$3.17 \times 10^{-10} \times \exp(-213.8/T)$
$N^+ + o-H_2$	→	$NH^+ + H$	$4.86 \times 10^{-10} \times \exp(-41.1/T)$
$^{15}N^+ + p-H_2$	→	$^{15}NH^+ + H$	$3.19 \times 10^{-10} \exp(-208.3/T)$
$^{15}N^+ + o-H_2$	→	$^{15}NH^+ + H$	$5.35 \times 10^{-10} \exp(-37.0/T)$
$N^+ + HD$	→	$ND^+ + H$	$4.77 \times 10^{-10} \exp(-50.1/T)$
$^{15}N^+ + HD$	→	$^{15}ND^+ + H$	$4.92 \times 10^{-10} \times \exp(-47.2/T)$

- Minor effect on NH/ND model predictions as NH(ND) principally produced from DR of N_2H^+ (N_2D^+)
- Similar NH_3 gas phase abundance (coming specifically from $N^+ + o\text{-}H_2$)
- Reduction of deuterated ammonia
- New experiments on $N^+ + HD$ welcome!
- Full theoretical treatment still to be done (introduction of the fine and electronic structure of NH^+)

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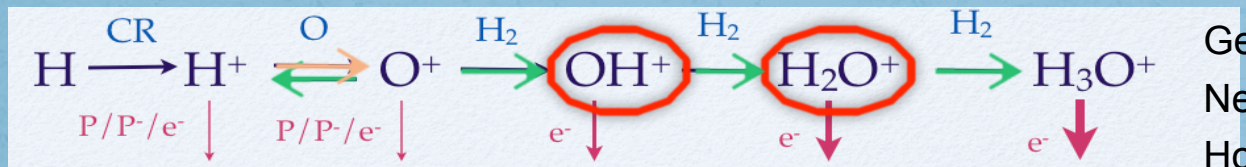
Ion molecule chemistry at work :
a measure of the cosmic ionization rate and molecular fraction

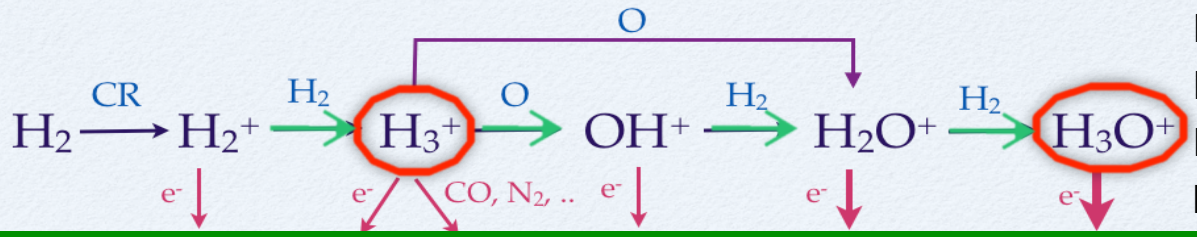
Oxygen chemistry

2 channels, 3 successive possible steps

diffuse



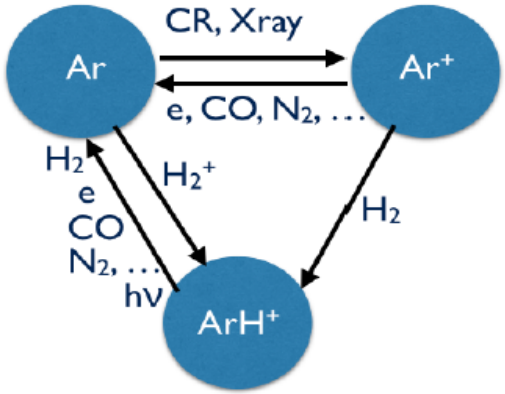
dense



Gerin et al. 2010, AA518, L110
Neufeld et al. 2010, AA521, L10
Hollenbach et al. 2012, ApJ754, 105
Indriolo et al. 2012, ApJ758, 83
Indriolo & McCall 2012, ApJ745, 91
Indriolo et al. 2015, ApJ800, 40
Le Petit et al. 2016, A&A585, A105

Well studied chemistry (see Indriolo et al. 2012) apart photodissociation of OH^+

ArH^+ chemistry



2channels, one single step

Schilke et al. 2014, AA 566, A29
Neufeld & Wolfire 2016, ApJ 826: 183

badly known:
RR of Ar^+ ($\neq$ collisional radiative recombination)
DR of ArH^+ (only upper limit)

Simplified chemical network

$H_2 + CR \rightarrow H_2^+ + e$	ζ_2	$dn(H_2^+)/dt = \zeta_2\, n(H_2)$
$H_2^+ + H_2 \rightarrow H_3^+ + e$	$k(H_2^+ \mid H_2)$	$dn(H_3^+)/dt = k(H_2^+ \mid H_2)\, n(H_2^+) n(H_2)$
		$= -\, dn(H_2^+)/dt$
$H_3^+ + e \rightarrow$ products	$k_e(H_3^+)$	$dn(H_3^+)/dt = -k_e(H_3^+)\, n(H_3^+)\, n_e$
$H + CR \rightarrow H^+ + e$	ζ_H	$dn(H^+)/dt = \zeta_H\, n(H)$
$O + H^+ \rightarrow O^+ + H$	$k(O \mid H^+)$	$dn(O^+)/dt = k(O \mid H^+)\, n(H^+) n(O)$
$O^+ + H_2 \rightarrow OH^+ + H$	$k(O^+ \mid H_2)$	$dn(OH^+)/dt = k(O^+ \mid H_2)\, n(O^+)\, n(H_2)$
		$= -dn(O^+)/dt$
$OH^+ + H_2 \rightarrow H_2O^+ + H$	$k(OH^+ \mid H_2)$	$dn(H_2O^+)/dt = k(OH^+ \mid H_2)\, n(OH^+)\, n(H_2)$
		$= -dn(OH^+)/dt$
$H_2O^+ + H_2 \rightarrow H_3O^+ + H$	$k(H_2O^+ \mid H_2)$	$dn(H_3O^+)/dt = k(H_2O^+ \mid H_2)\, n(H_2O^+)\, n(H_2)$
		$= -dn(H_2O^+)/dt$
$OH^+ + e \rightarrow O + H$	$k_e(OH^+)$	$dn(OH^+)/dt = -k_e(OH^+)\, n(OH^+)\, n(e)$
$H_2O^+ + e \rightarrow$ products	$k_e(H_2O^+)$	$dn(H_2O^+)/dt = -\, k_e(H_2O^+)\, n(H_2O^+)\, n(e)$
$H_3O^+ + e \rightarrow$ products	$k_e(H_3O^+)$	$dn(H_3O^+)/dt = -\, k_e(H_3O^+)\, n(H_3O^+)\, n(e)$

Ion molecule chemistry at work : a measure of the cosmic ionization rate and molecular fraction

Steady state analysis (Indriolo et al. 2015)

- From H_3^+ chemistry: $\zeta_2 = x_e \; k_e(H_3^+) \; n_H \; \frac{n(H_3^+)}{n(H_2)}$ with $x_e = \frac{n(e)}{n_H}$ and ζ_2 CR ionization of H_2

- From OH^+, H_2O^+ chemistry: $f_{H_2} = \frac{2 x_e k_e(H_2O^+)/k(OH^+ \mid H_2)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2)}$

where $f_{H_2} = \frac{2 \times n(H_2)}{n(H) + 2 \times n(H_2)} = \frac{2 \times n(H_2)}{n_H}$ (≠ from Wiesemeyer et al. 2016)

Defining ε as the ratio of the OH^+ production rate to the cosmic ray ionization rate

$$\epsilon\zeta_H = \frac{N(OH^+)}{N(H)} n_H \left[\frac{f_{H_2}}{2} k(OH^+ \mid H_2) + x_e k_e(OH^+) \right]$$

ε accounts for the fact that not every instance of hydrogen ionization results in the formation of OH^+ due to $O^+ + H \rightarrow O + H^+$ and H^+ recombination (Neufeld et al. 2010)

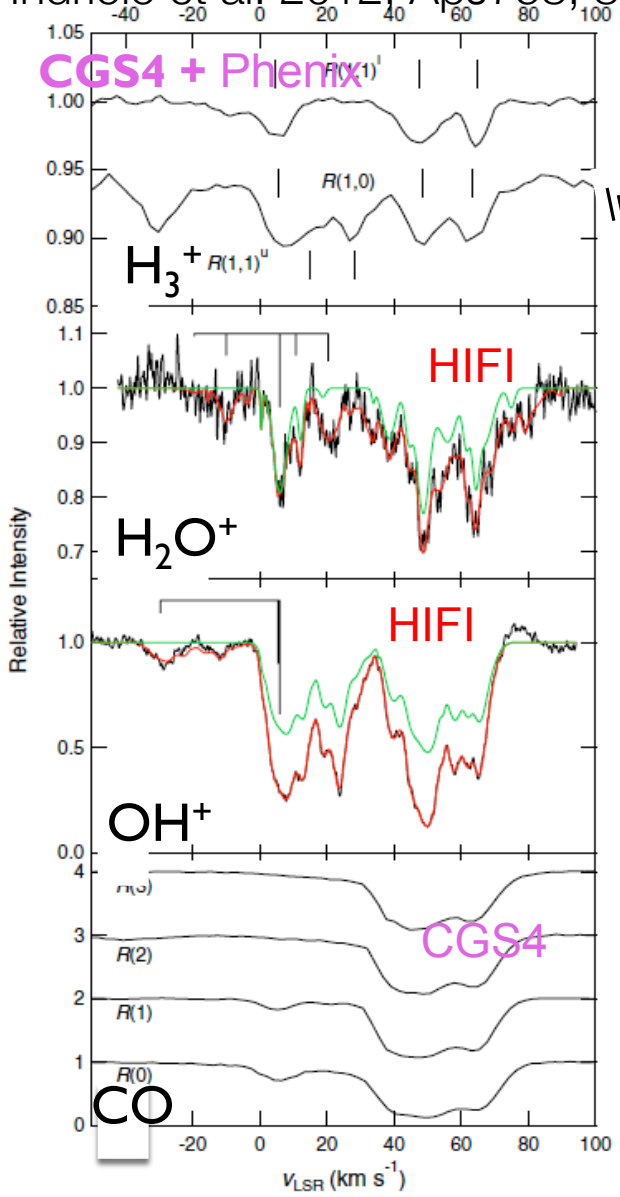
Assuming $\zeta_2 \approx 2 \times \zeta_H$

$$\epsilon\zeta_2 = \frac{N(OH^+)}{N(H)} 2 \times n_H \times x_e \left[\frac{k_e(H_2O^+)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2)} + k_e(OH^+) \right]$$

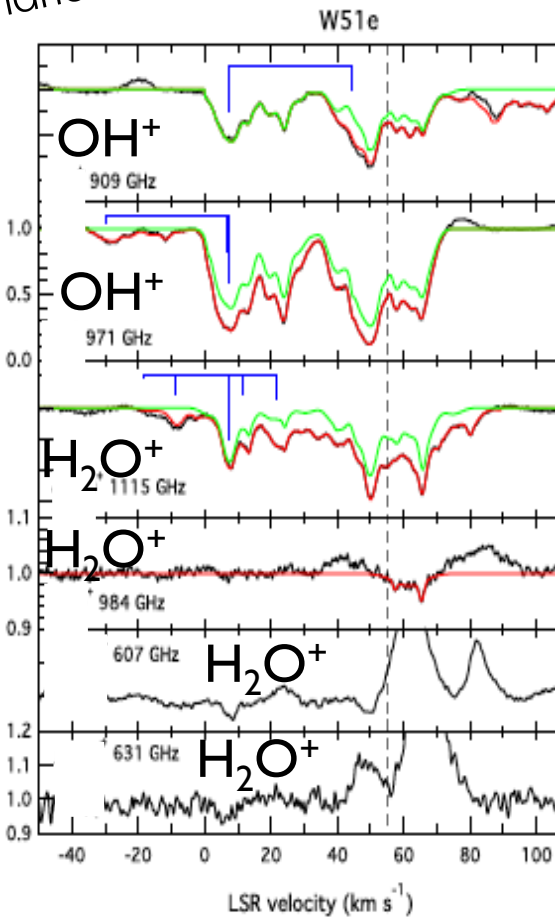
Analysis requires estimates of x_e, ε, T, n_H, + observations of OH^+, H_2O^+, H (see talk of N. Indriolo)

Example of W51 (1)

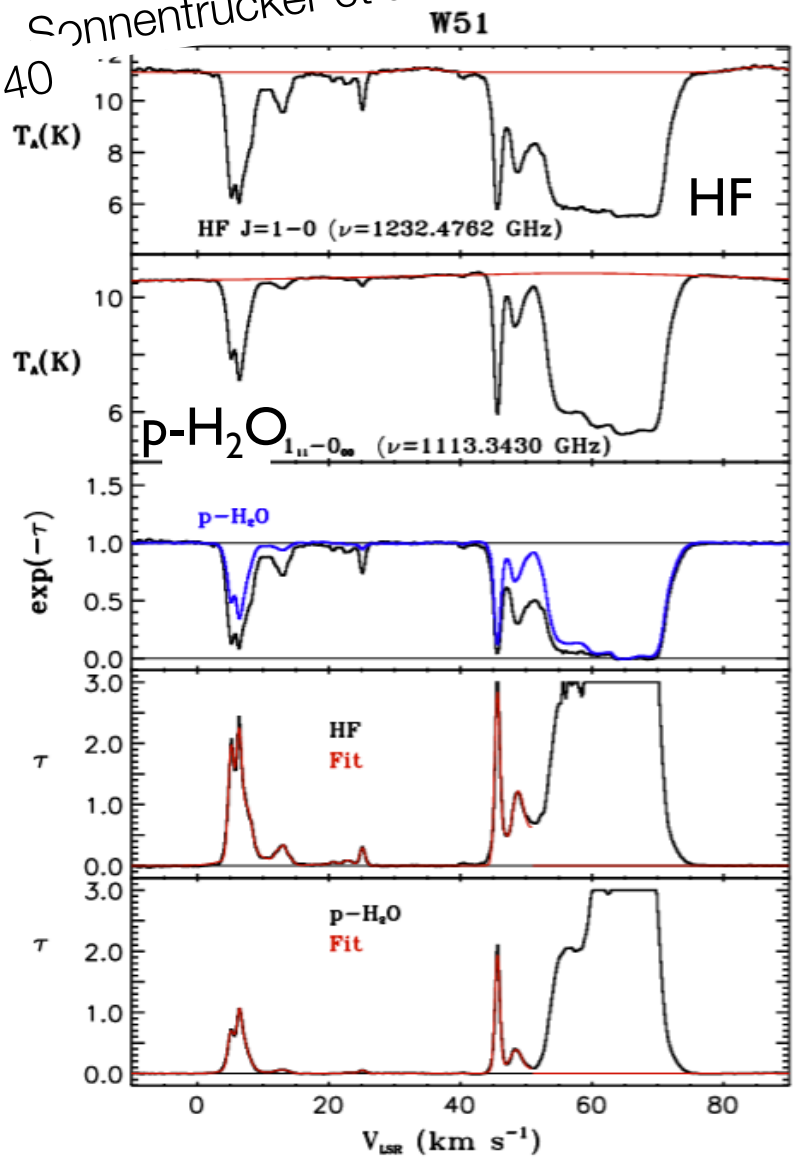
Indriolo et al. 2012, ApJ758, 83



Indriolo et al. 2015, ApJ 800, 40



Sonnentrucker et al. 2015, ApJ 806,49



Example of W51 (2)

1. Diagnostics of the cosmic ionization rate

Molecular and Atomic Abundances in the Diffuse Cloud toward W51

Species	$N(X)$ (cm^{-2})	v_{LSR} (km s^{-1})	FWHM (km s^{-1})	References
H	$(1.39 \pm 0.3) \times 10^{21}$	6.2	5.6	1
H_2	$(1.06 \pm 0.52) \times 10^{21}$	3–10	...	2
H_3^+	$(2.89 \pm 0.37) \times 10^{14}$	5.0	10.5	3
OH^+	$(2.97 \pm 0.13) \times 10^{13}$	0–11	...	3
H_2O^+	$(6.09 \pm 0.96) \times 10^{12}$	0–11	...	3
C^+	$(4.0 \pm 0.4) \times 10^{17}$	0–11	...	4
CH	$(3.7 \pm 0.2) \times 10^{13}$	3–10	...	5
CO	$(2.81 \pm 0.21) \times 10^{15}$	4.8	9.6	3

Indriolo et al. 2012, ApJ 758, 83

+ N(HF) $(1.63 \pm 0.12) \times 10^{13}$ cm^{-2}
Sonnentrucker et al. 2015

Steady state formulae + guessed x_e
from C^+ : $C^+ / n_H \approx x_e$

from H_3^+

Indriolo et al. 2012:
$\zeta_2 \approx (4.8 \pm 3.4)\ 10^{-16}\ s^{-1}$

from OH^+

Indriolo et al. 2015 :
$\varepsilon \approx 0.07$
$\zeta_2 \approx (5.6 \pm 1.0)\ 10^{-16}\ s^{-1}$ in the (4, +11 km/s) VLSR range
Different ζ_2 for different velocity ranges

mean value of the cosmic ionization rate outside the Galactic center $\zeta_2 \approx 3.6\ 10^{-16}\ s^{-1}$ (Indriolo et al. 2015)

ζ_2 significantly larger than previously thought

Hartquist, Black & Dalgarno 1978 (MNRAS 185, 643) derived $\zeta_2 \approx 5\ 10^{-17}\ s^{-1}$ from OH and HD in diffuse clouds

Example of W51 (3)

2. Diagnostics of the molecular fraction

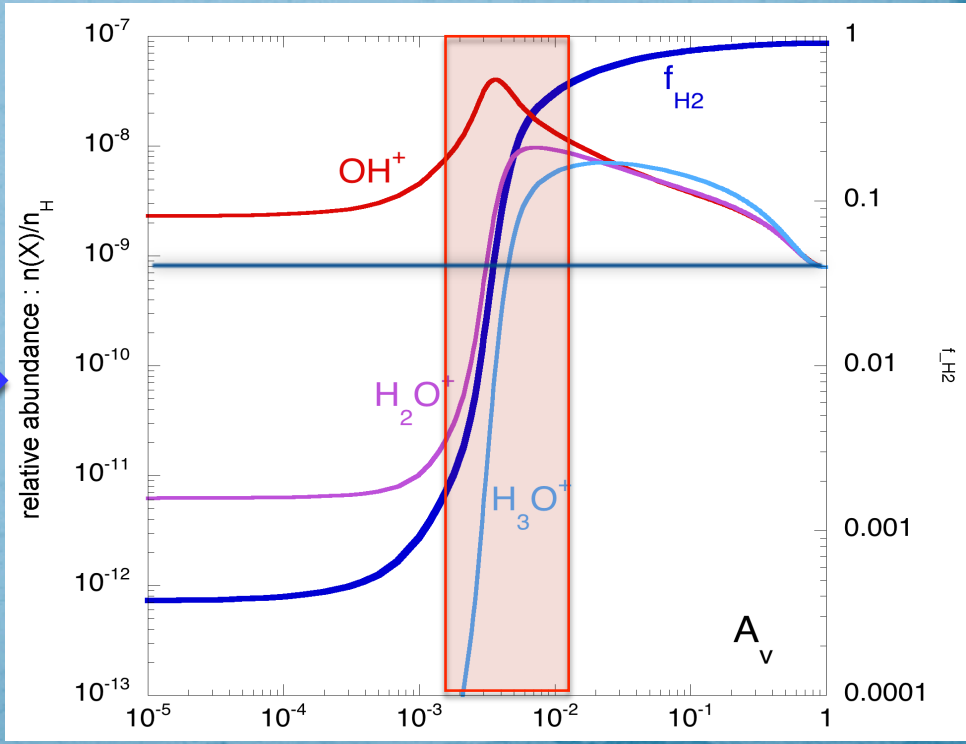
Steady state formulae + guessed x_e :

$$f_{H_2} = \frac{2x_e k_e(H_2O^+)/k(OH^+ \mid H_2)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2)}$$

$f_{H_2} = 0.04 \pm 0.01$ from OH^+, H_2O^+ towards W51

✏ The derivation of the molecular fraction from OH^+/H_2O^+ is a signature of its value at the formation peak.

n_H=50 cm^{-3}, ζ_2 = 5x10^{-16} s^{-1}, χ = 1, A_{vtot} = 2



Meudon PDR code model
Similar results reported in Hollenbach et al. 2012, ApJ 754, 105, Indriolo et al. 2015

Example of W51 (4)

Diagnostics of the molecular fraction

Steady state formulae + guessed x_e :

$$f_{H_2} = \frac{2 x_e k_e(H_2O^+)/k(OH^+ \mid H_2)}{N(OH^+)/N(H_2O^+) - k(H_2O^+ \mid H_2)/k(OH^+ \mid H_2)}$$

$f_{H_2} = 0.04 \pm 0.01$ from OH^+, H_2O^+ towards W51

From the observations of HI 21cm and proxies of H_2: CH, HF

$N(CH)/N(H_2) = 3.6\ 10^{-8}$ (Sheffer+ 2008, ApJ 687, 1075)

$N(HF)/N(H_2) \approx 1.2\ 10^{-8}$ (Indriolo+ 2013, ApJ 764, 188, Sonnentrucker+ 2015, ApJ 806, 49)

N(H) (cm^{-2})	$1.4\ 10^{21}$	N(H_2) (cm^{-2})	f
N(CH) (cm^{-2})	$3.7\ 10^{13}$	$1.0\ 10^{21}$	0.6
N(HF) (cm^{-2})	$1.6\ 10^{13}$	$1.3\ 10^{21}$	0.75

Example of W51 (5)

Diagnostics of the molecular fraction

Steady state formulae + guessed x_e :

$$f_{\mathrm{H_2}} = \frac{2 x_e k_e(\mathrm{H_2O^+})/\mathrm{k}(\mathrm{OH^+} \mid \mathrm{H_2})}{N(\mathrm{OH^+})/\mathrm{N}(\mathrm{H_2O^+}) - \mathrm{k}(\mathrm{H_2O^+} \mid \mathrm{H_2})/\mathrm{k}(\mathrm{OH^+} \mid \mathrm{H_2})}$$

$f_{\mathrm{H_2}} = 0.04 \pm 0.01$ from $\mathrm{OH^+}, \mathrm{H_2O^+}$ towards W51

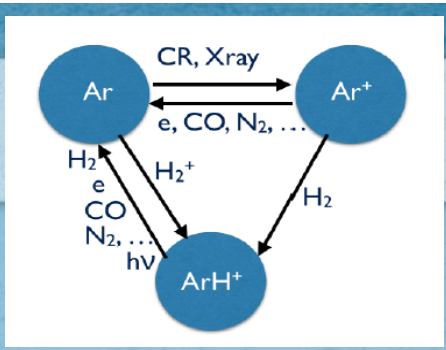
From the observations of HI 21cm and proxies of H_2: CH, CF

$f_{\mathrm{H_2}} \sim 0.6 - 0.7$

✏ The molecular fraction obtained from observations of H and proxies of H_2 involves the integration over the cloud

see also discussion in Le Petit et al. 2016, AA585, A105

ArH^+ chemistry (1)



Surprise! First rare gas containing molecule
Schilke et al. 2014, AA566, A29

$^{36}ArH^+$ and $^{38}ArH+$ isotopes detected also at z=0.89 in absorption toward PKS1830-211 (Müller et al. 2015, A&A582, L4)

Transition shifted towards 350GHz

Detectable then from ground with ALMA.

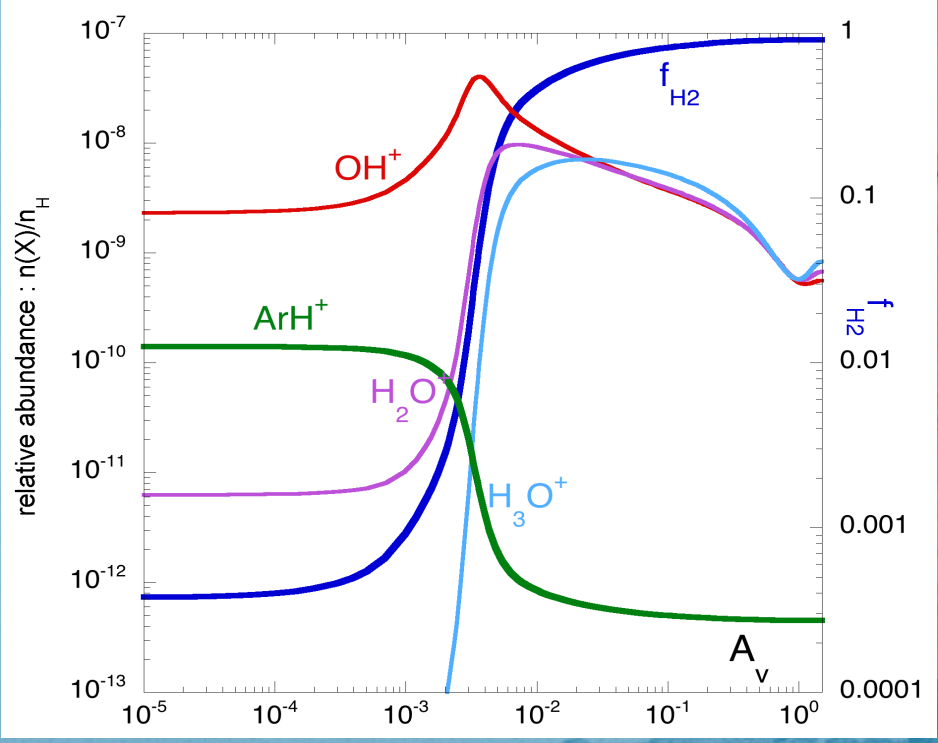
Extensive grid of diffuse cloud models reported in Neufed + Wolfire 2016,
ApJ 826, 183 (talk of M. Wolfire)

ArH^+ essentially present in atomic gas

No single set of cloud parameters provides an acceptable fit to the observed abundances of ArH^+, OH^+, H_2O^+

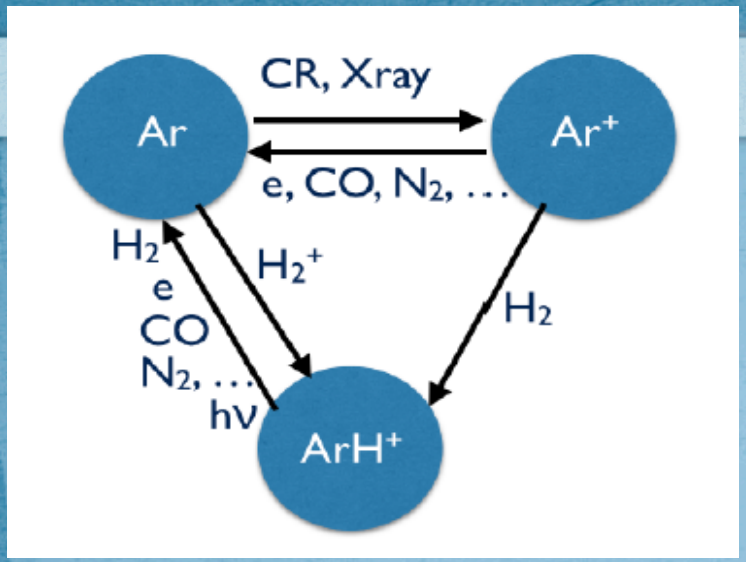
2 components model may be appropriate (cf talk of M. Wolfire)

n_H=50 cm^{-3}, χ = 1, ζ_2 = 5x10^{-16} s^{-1}, A_{vtot} = 3



Meudon PDR code model

ArH^+ chemistry (2)



🚩 ArH^+ essentially in atomic gas

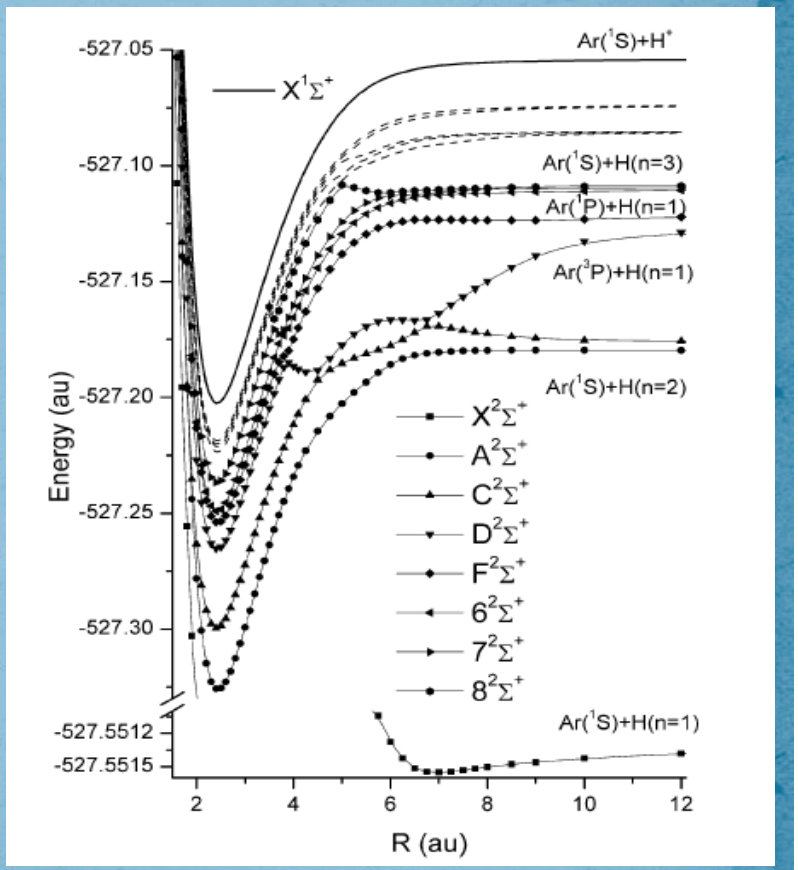
→ **Even simpler reaction schema** (Ar, Ar^+, H_2, H_2^+, O, C)

Slow photodissociation (Alekseev+2007, Roueff+2014)

H?, He^+? Exothermic charge exchange not included in the chemistry of Schilke+ 2014

Recombination of Ar^+ (formula of Shull and van Steenberg based on formulae extrapolation). Not available from Badnell recent data base.

Dissociative recombination: upper limit available only from experiments Mitchell et al. 2005, J. Phys. B 38, challenge for theorists; no favorable crossing for recombination



Kirrander et al. 2006, PCCP 8, 247

Physics, chemistry and excitation of hydride molecules

Introduction

Molecular and thermochemical properties

Some illustrations of the interplay between observations and chemical mechanisms

- New analysis of the $N^+ + H_2$ reaction and its isotopic variants
- Tracers of atomic gas: OH^+ / ArH^+
- Tracers of molecular gas : H_3^+, CH, HF

Examples of (photo)chemical excitation (OH, H_3O^+, NH_3)

Summary

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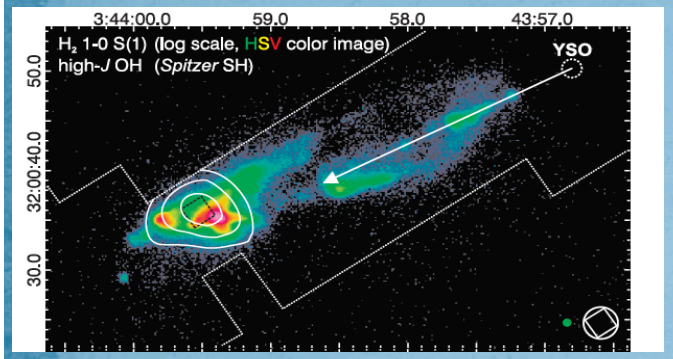
l'Observatoire de Paris | LERMA

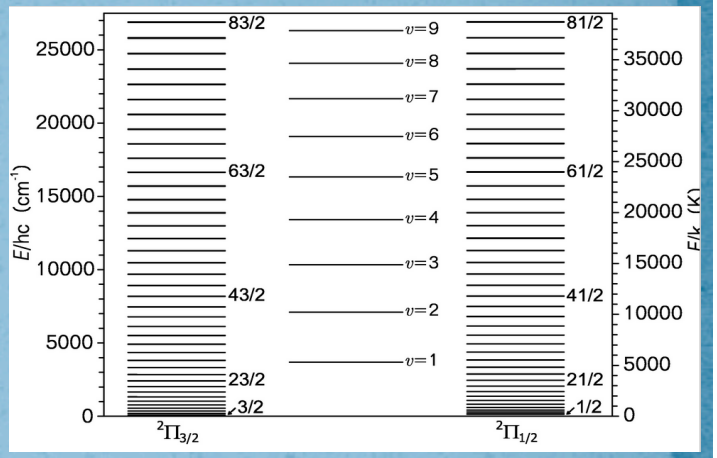
Laboratoire d'Étude du Rayonnement et de la Matière en Astrophysique et Atmosphères

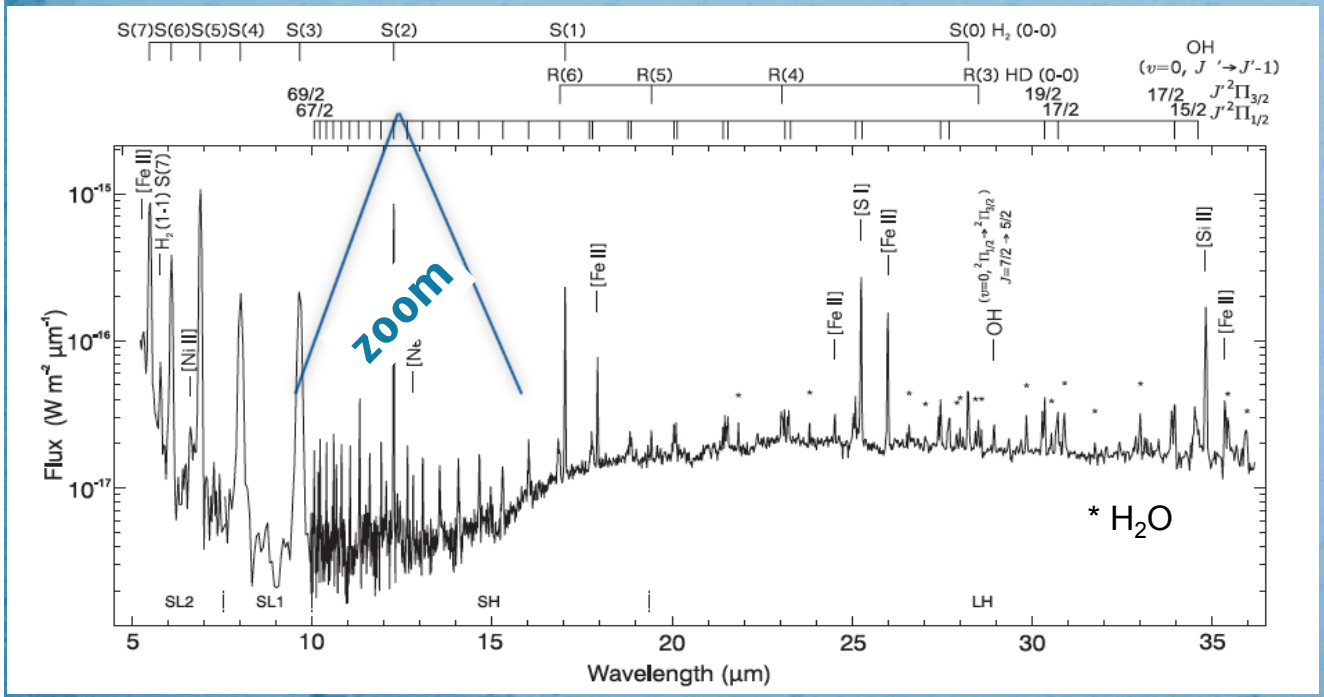
Paris, December 12, 2016

Suprathermal excitation of OH in the HH 211 outflow (1)



SPITZER Space Telescope observations
Tappe et al. ApJ680, L117, 2008
Tappe et al. ApJ751:9, 2012
OH and H_2O emission present in the terminal shock region





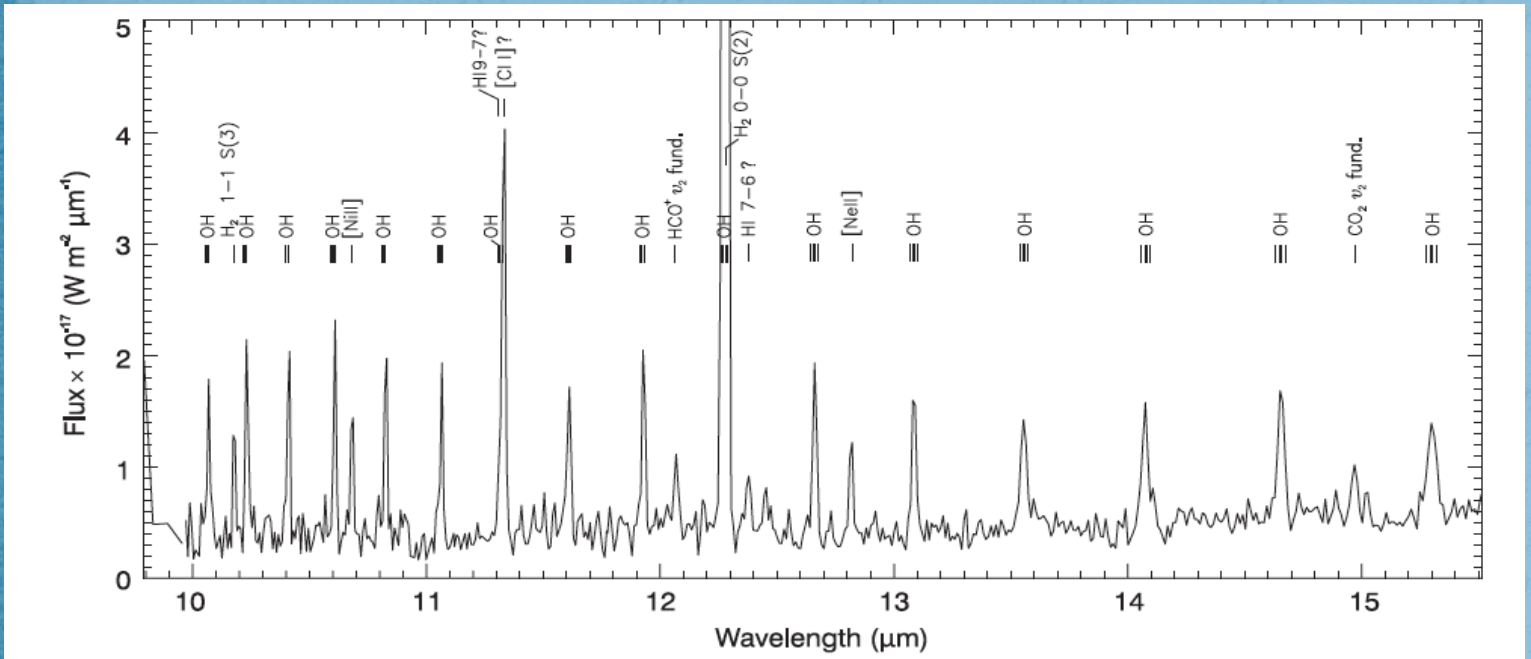
Pure rotational : H_2, HD, H_2O

Highly excited levels of OH $E_{up} \approx$ 28200K above ground state

OH also populated at lower excitation as shown by intersystem transitions;

no convincingly vibrationally excited transition detected.

Suprathermal excitation of OH in the HH 211 outflow (2)



IRS spectrum of the terminal shock Tappe et al. 2012

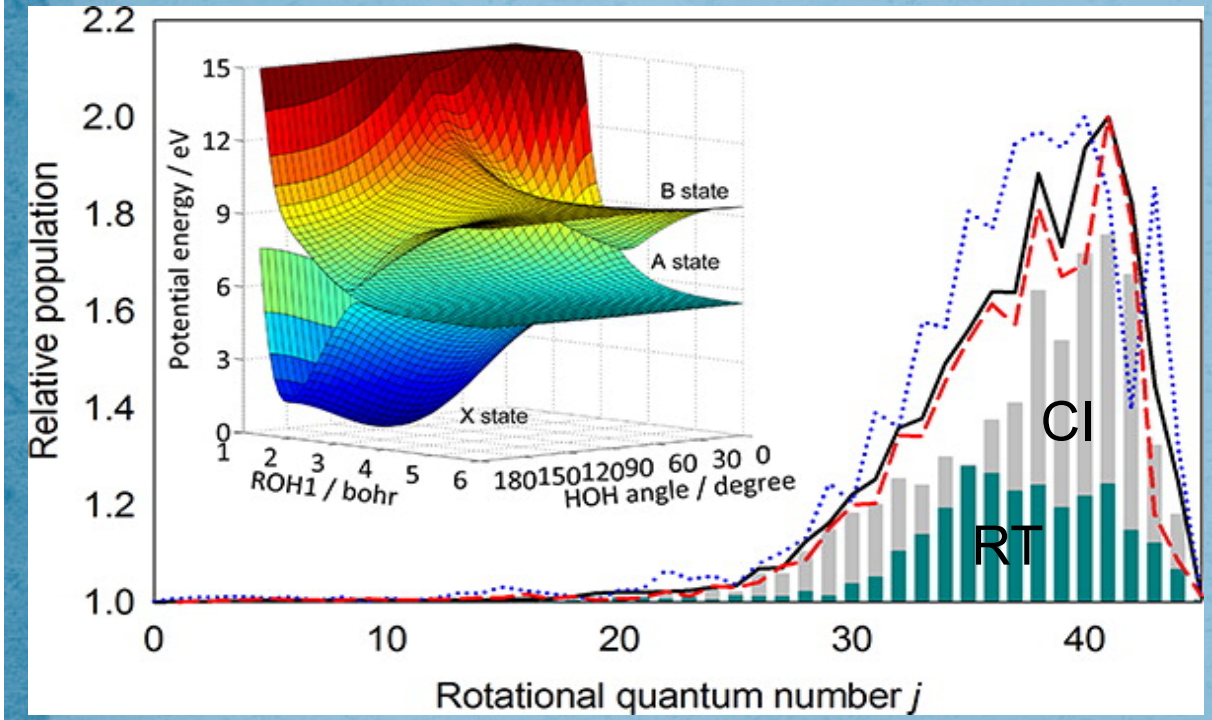
Higher possibly present excited transitions below 10μ not available in the IRS spectrum

- **Selective non thermal excitation of OH**
  - A Einstein coefficient of high J transitions ≈ 10 - 400 s^{-1} compared to H_2O
  - A values of a few x 10^{-3} s^{-1} and H_2 A values of 3 10^{-11} – 3 x 10^{-7} s^{-1}
  - too large critical densities for OH
- **Shock chemistry ?**
  - ≈ 29000 K endothermicity required to populate OH (J=63) : much larger than typical neutral fluid temperature

Suprathermal excitation of OH in the HH 211 outflow (3)

possible role of H_2O photodissociation

photodissociation of H_2O through photons with E>9eV leads to ground state OH with high rotational excitation



Zhou et al. 2013, *J. Phys. Chem. A* 117, 6940
Guo & Yarkony 2016, *PCCP* 18, 26335

Experiments :
weak featureless band at 7.4eV + structured emission at 9.5 eV (Cheng et al. 2011 JCP134, 06431)

Theory : The photodissociation of H_2O in its B band is a *prototype* for nonadiabatic reaction dynamics.

In addition to dissociation via the adiabatic pathway to the $OH(\tilde{A}^2\Sigma+) + H$ fragments, it also produces the $OH(X\,^2\Pi) + H$ fragments through two nonadiabatic pathways:
the $\tilde{B} \rightarrow X$ transition via two conical intersections (CI) and the
$\tilde{B} \rightarrow \tilde{A}$ transition via a Renner - Teller (RT) pair.

Suprathermal excitation of OH in the HH 211 outflow (4)

- **Proposed scenario:**

  UV-induced photodesorption of water ice from grain mantles and photodissociation of H_2O either in the gas phase or directly in the grain ice mantles are the primary sources of OH and H_2O.

  Lyα-dominated FUV radiation coming from a radiative shock; assumed x-section: 8×10^{-18} cm^2, photodesorption yield of 3-5 x 10^{-3}.

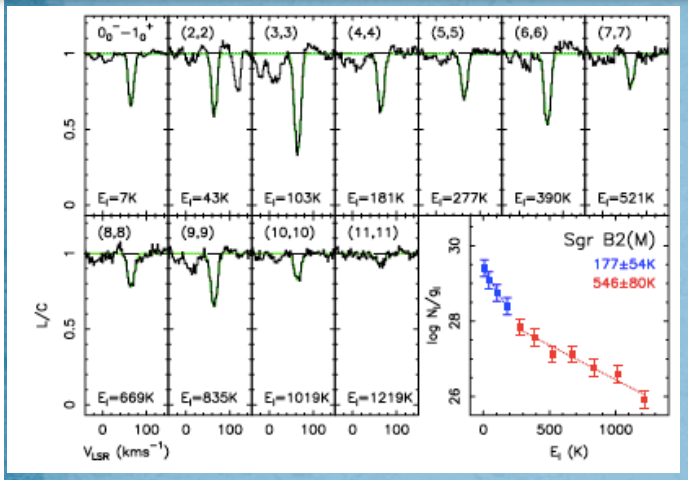
  include other molecular emissions (HCO^+, HCN, (v=1-0) CO, …)

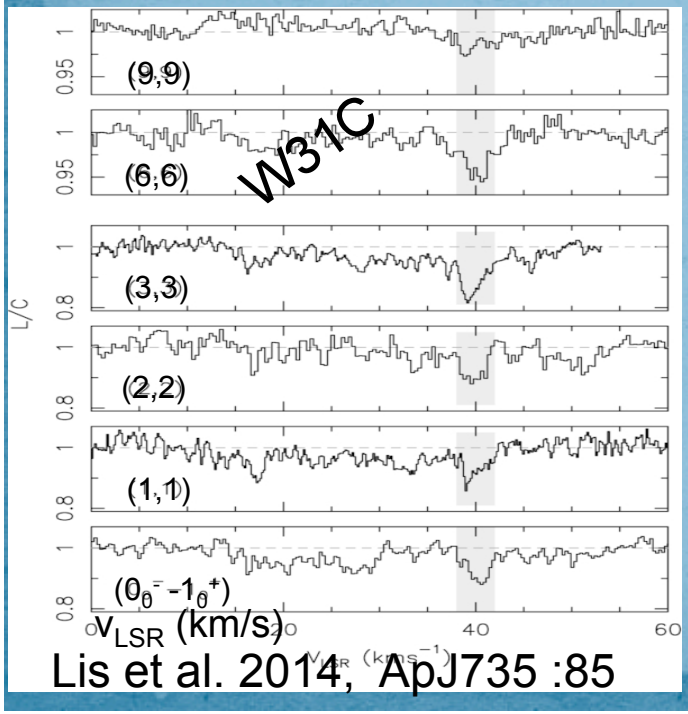
  a nice challenge for future model

- **Other sources with high J excited OH**: TW Hya, other outflows (Tappe et al. 2012)

- **similar mechanism** invoked in the observed prompt visible A-X emission of OH in comet Hyakutake (A Hearn et al. 2015, ApJ 150:5)

Widespread rotationnaly hot H_3O^+ in the Galactic ISM





Lis et al. 2014, ApJ735 :85

Inversion transitions; A values between a few x 10^{-2} and 10^{-1} s^{-1}

Galactic Center: highly excited NH_3 also detected presence of warm gas

W31C : quiescent environment

chemical pumping scenario formation :

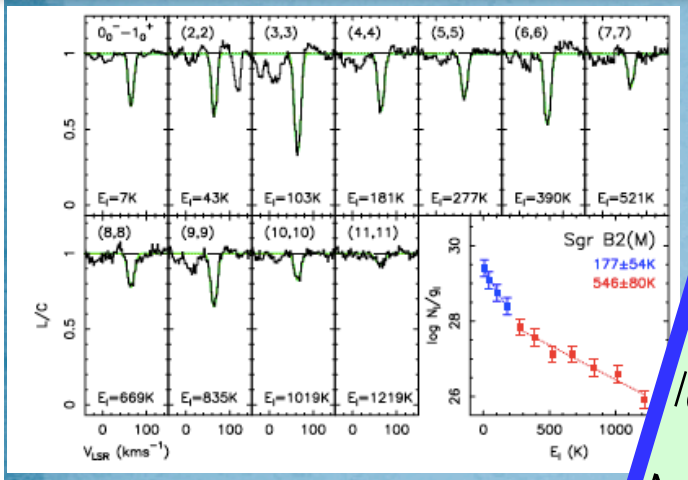
$H_2 + H_2O^+ \rightarrow H_3O^+ + H \quad \Delta E \approx 1.7eV$

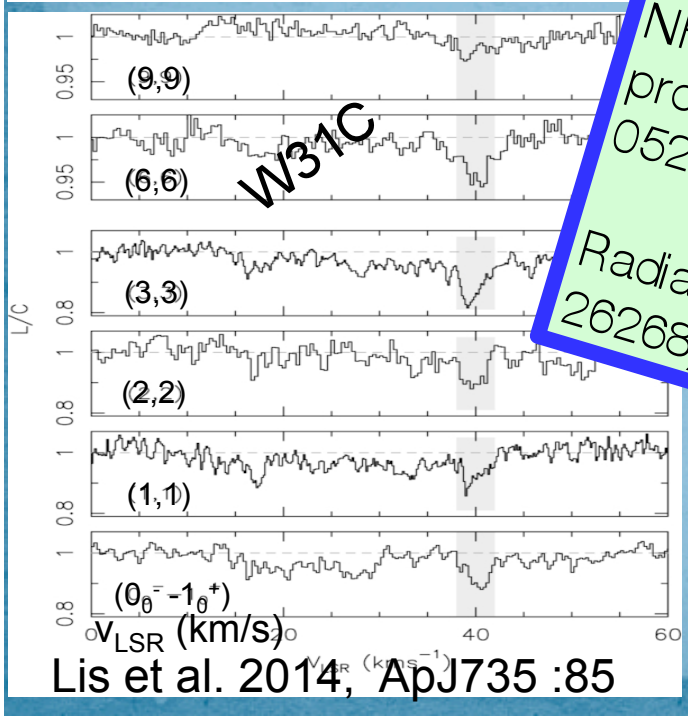
wich fraction into internal energy?

Highly excited non metastable levels relax rapidly to metastable levels (lower J=K) by spontaneous emission. Populations partially redistributed by inelastic collisions and background IR continuum radiation.

Destruction rapid through DR : $k_e \approx 10^{-6}$ n_e

Widespread rotationnaly hot H_3O^+ in the Galactic ISM





Lis et al. 2014, ApJ735 :85

probable close coupling between excitation and chemistry; model in progress?

Collision rates not available for highly excited NH_3 (possible proxy of H_3O^+) nor for H_3O^+

Difference between reported energies of highly excited NH_3 levels in JPL and SLAIM data bases.

NH_3 and H_3O^+ sensitivity coefficients for probing a variable proton to electron mass ratio (Owens et al 2016, PRA93, 052506; 2015, MNRAS 454, 22920)

Radiative cooling of H_3O^+ (Melnikov et al. 2016, PCCP 18, 26268)

...s: A values between a few x 10^{-2}

...detected

...astic

collisions and ...

Destruction rapid through ...

Summary (1)

- basic thermochemical properties provide the general frame of the chemical processes at work
- Hydride families, supposedly involving simple formation reactions (with H_2), are very diverse and allow to address different aspects
  - atomic gas
  - molecular proxy
  - warm environments
  - probe of ionization sources
  - photochemistry
  - anomalous excitation resulting from photo-chemical mechanisms
- dedicated studies of elementary reactions
  - the case of $N^+ + H_2$: a nice example of state to state chemistry
  - not yet fully understood
- full understanding requires complementary information from other molecules

Summary (2)

Density diagnostics: atomic / molecular	HI, OH^+, ArH^+/ CH, HF
Warm environments shocks turbulent Photons / X rays	endothermic reactions OH, H_2O, CH^+, SH^+
Source of ionization: UV / CR / Xrays coupling to magnetic field	C, S, Cl chemistries / H_3^+, OH^+, H_2O^+, ArH^+
State to state chemistry : ortho/para	Role of internal energy H_2, H_2O, H_2O^+, NH_2 Nuclear spin dynamics in water ice
Role of surface processes	H_2O Sulfur chemistry

Thanks to all collaborators

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Jacques Le Bourlot, Observatoire de Paris
Franck Le Petit, Observatoire de Paris
Darek Lis, Observatoire de Paris
Jean Christophe Loison, Université de Bordeaux
Ronald McCarroll, UPMC and Observatoire de Paris

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