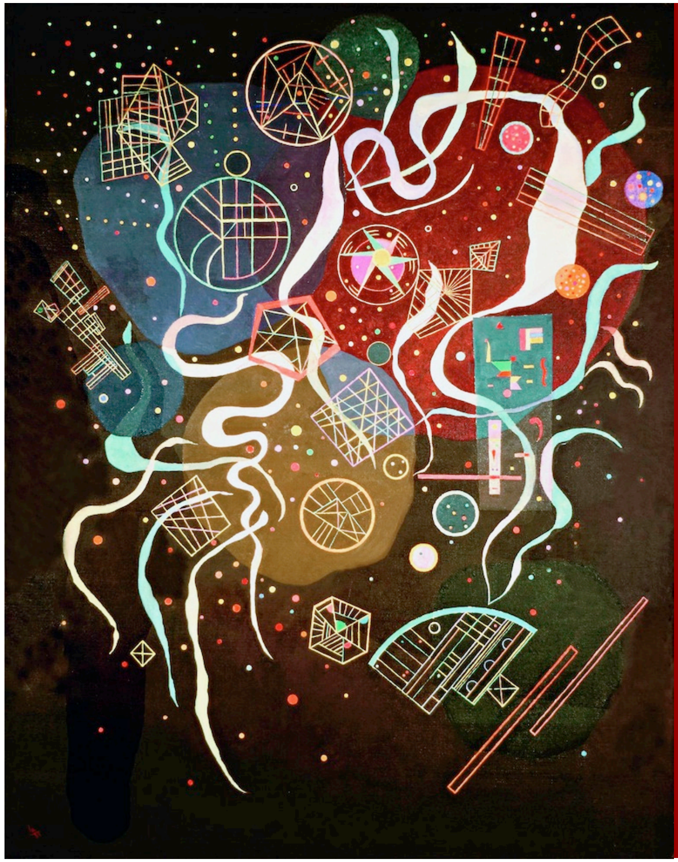

State-to-state reactive and inelastic collisions involving hydrides

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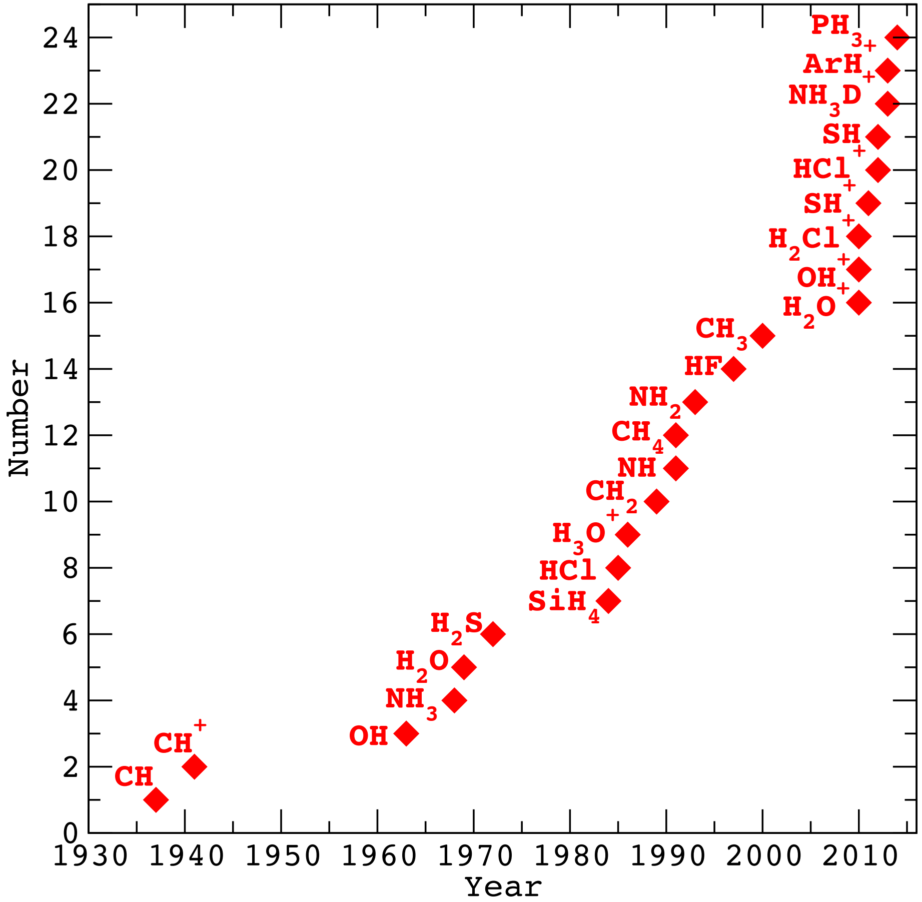
The hydride toolbox, Paris, 12-15 December 2016

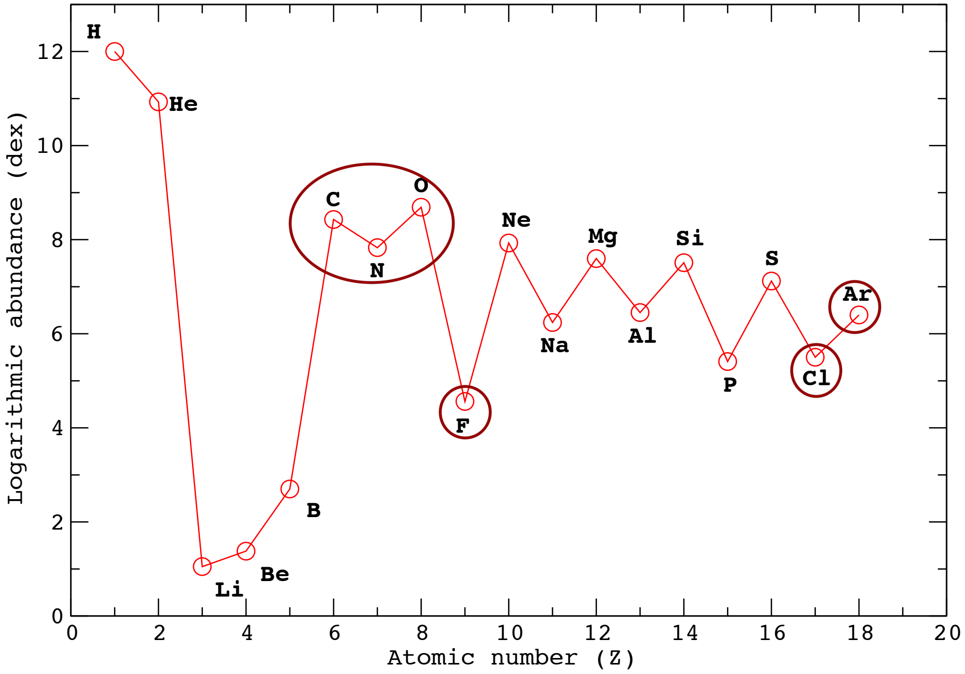
Motivation



Interstellar and circumstellar hydrides,
from http://www.astrochymist.org/

- Hydrides have high critical densities (>10^6 cm^{-3})
- « Sub-thermal » excitation is the rule
- State-specific reactive processes compete with energy transfer processes

Outline



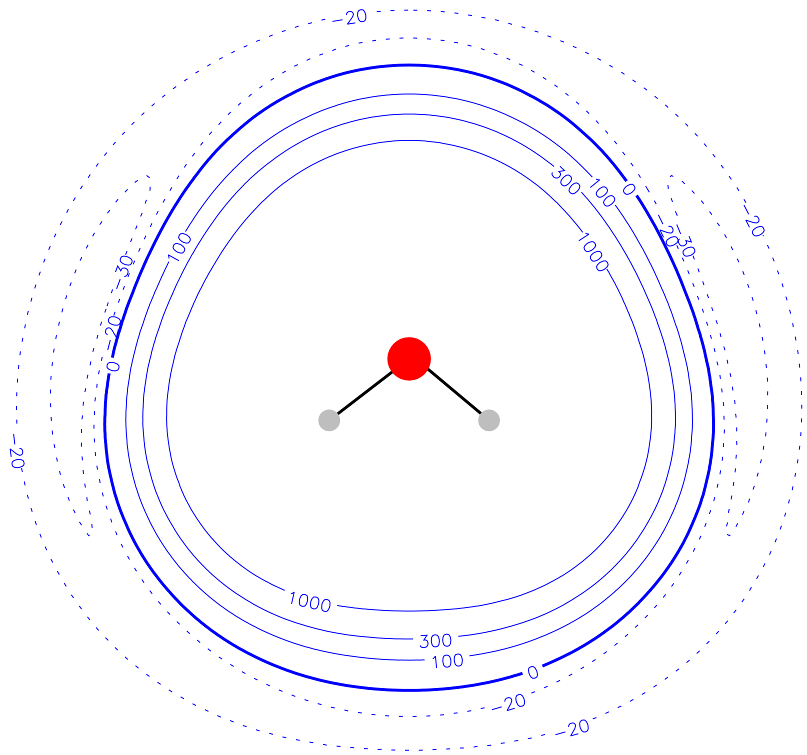
Solar photospheric abundances
Adapted from Asplund et al. ARAA 47 581 (2009)

- Carbon
  - CH^+, CH
- Nitrogen
  - NH_2, NH_3
- Oxygen
  - H_2O, OH, OH^+
- Halogen
  - HCl
- Noble gas
  - ArH^+

Colliders in the ISM

He	can be important but never dominant
H_2	most important in well-shielded molecular clouds
H	important behind dissociative shock fronts and PDRs
e^-	important in PDRs, especially for polar species

Molecular energy transfer



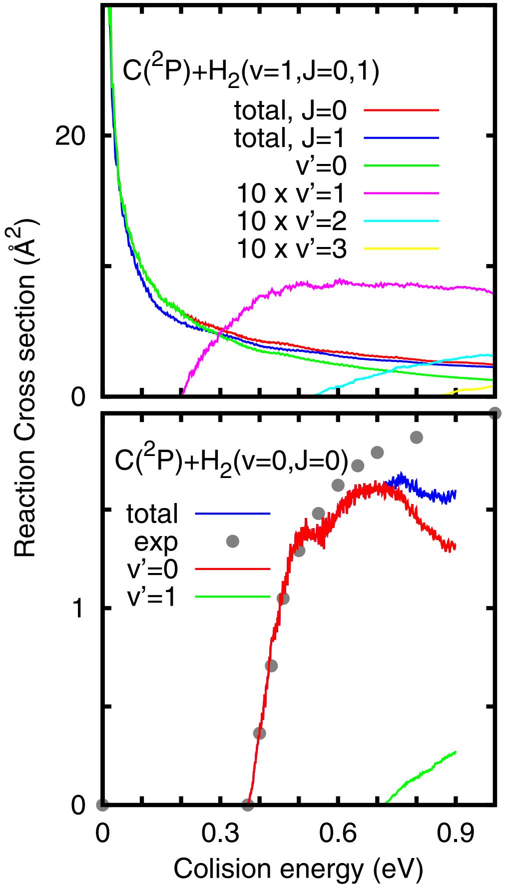
The H_2O-H_2 potential energy surface

- Scattering theory (BO approximation)
  - Electronic Schrödinger equation
  - Nuclei dynamics
- Experiment
  - Crossed molecular beams
  - Double resonance technique
  - Ion trap experiments

Carbon

CH^+ formation

$C^+(^2P) + H_2(v, j) \rightarrow CH^+(X^1\Sigma^+, j') + H$

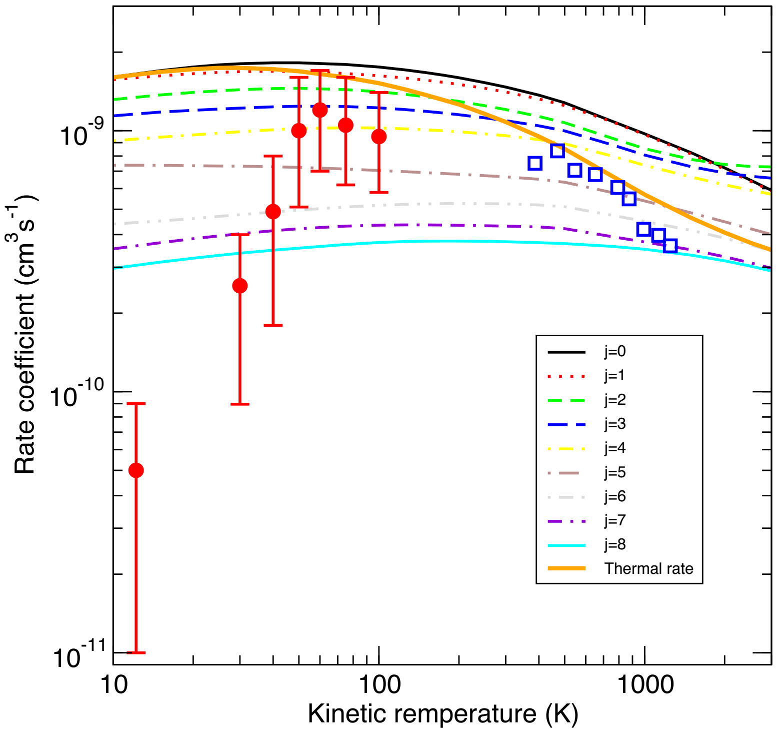


Zanchet et al. ApJ (2013)

- Endothermic with $H_2(v=0)$
- Wavepacket calculations by Roncero's group, in agreement with measurements with H_2 in $v=0$ and $v=1$
- CH^+ is formed rotationally hot, with a broad rotational distribution

CH^+ destruction

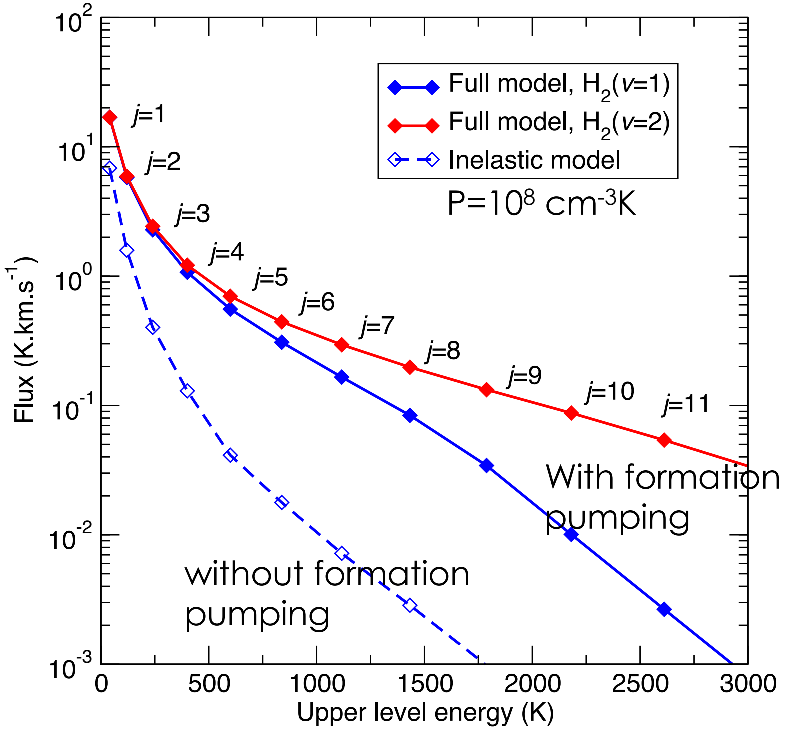
$CH^+(X^1\Sigma^+, j) + H \rightarrow C^+(^2P) + H_2$



Werfelli et al. J Chem Phys 143 114304 (2015)
Faure et al. to be submitted

- QCT and quantum calculations by Halvick and coworkers
- Measurements by Plasil et al. (2013), in contradiction with theory at *T*<50K
- Electron-impact dissociative recombination: see talk by Ioan Schneider

CH$^+$ emission in PDRs

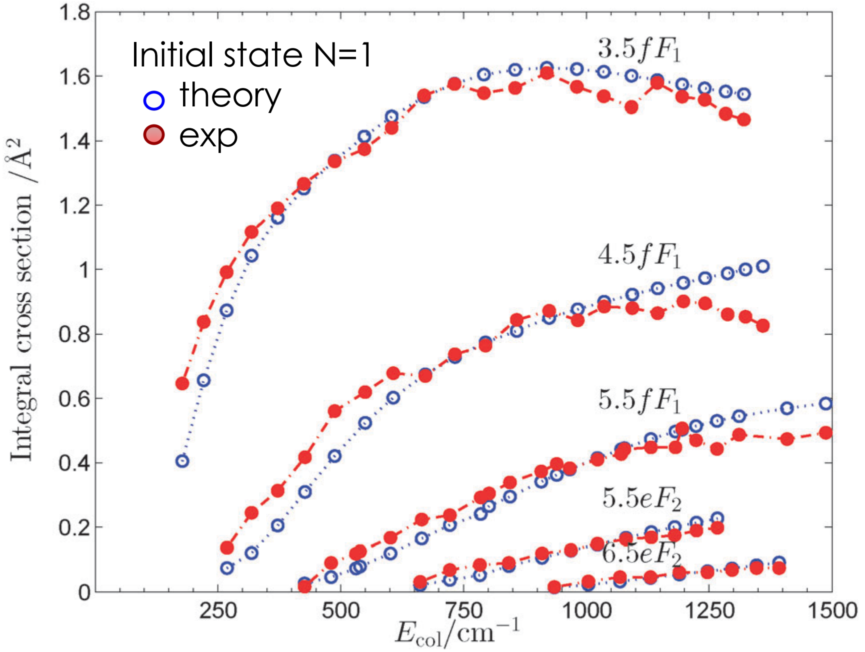


Faure et al. to be submitted

- Formation pumping is crucial for short-lived species (Black 1998, Godard & Cernicharo 2013)
- High-*j* transitions (*j*≥2) are pumped by $C^+ + H_2(v>0)$
- See talk by Anna Parikka

CH excitation

CH($X^2\Pi$, j) + He → CH($X^2\Pi$, j') + He



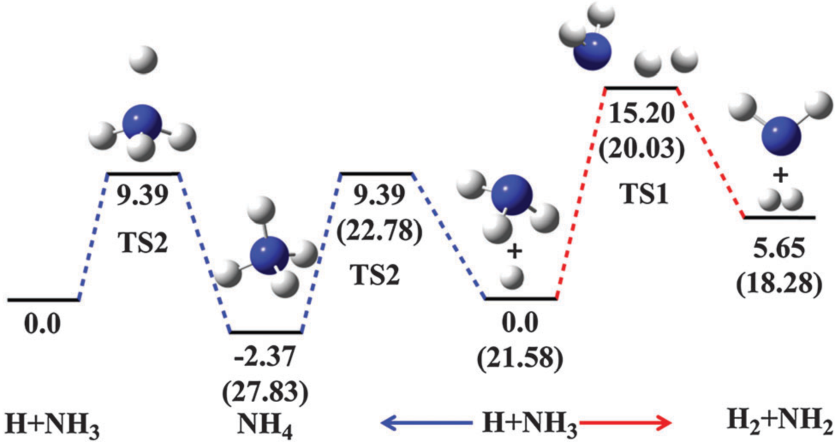
Marinakis et al. Phys Chem Chem Phys (2015)

- Experiments by McDonald & Liu (1989, 1990) on CH-He, CH-H2, CH-D_2
- Propensity rules due to parity and symmetry properties of Λ-doublets
- Collisions with H_2 can form $(CH_3)^*$. Quantum statistical calculations performed by Dagdigian (2016)

Nitrogen

NH_2 excitation

$NH_2(j_{kakc}) + H_2 \rightarrow NH_2(j'_{k'ak'c}) + H_2$

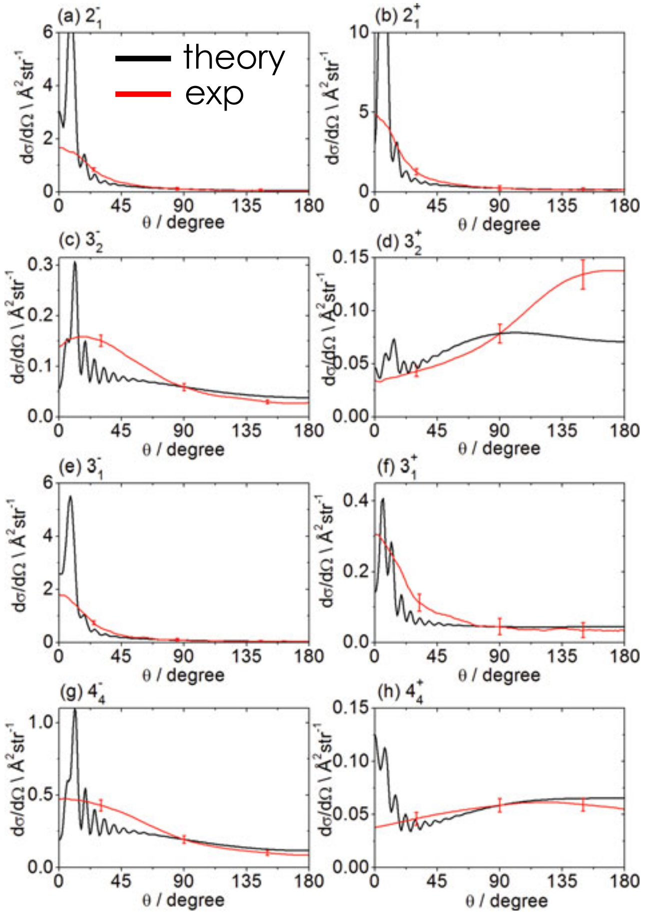


Li & Guo Phys Chem Chem Phys (2014)
Bouhafs et al. submitted to J Cherm Phys

- The exothermic reactive channel (NH_3+H) has a barrier of 4800K
- The full-dimensional PES was adapted for rigid-rotor calculations
- Transitions with Δk_c=0 favored, in contrast to radiative selection rules

NH_3 excitation

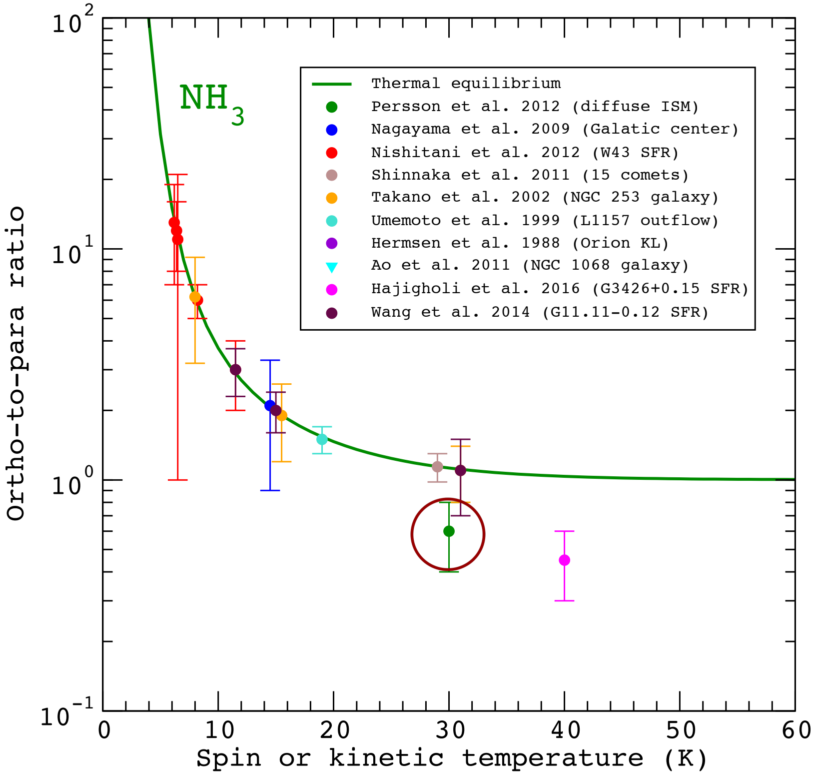
$NH_3(1_1^-) + nH_2 \rightarrow NH_3(j'k') + nH_2$ @580cm^{-1}



Tkac et al. Mol. Phys. (2015)

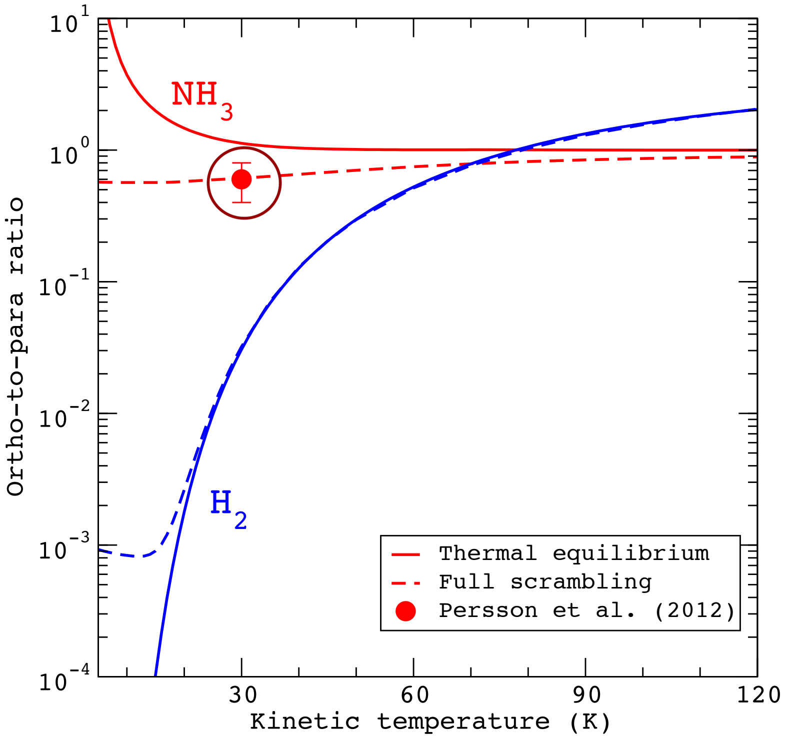
- Differential cross sections measured in crossed molecular beams
- The good agreements with theory provide a crucial test of the NH_3-H_2 PES of Maret et al. (2009)
- Full set of new data for NH_3-H_2 and NH_3-H available soon (Rist et al. to be submitted)

NH_3 ortho-to-para ratio



- Ortho-to-para ratios (OPR) can be related to a *formation* temperature
- Anomalous OPR for NH_3 (<1) measured with Herschel (Persson et al. 2012)
- Is the deficit of oNH_3 due to nuclear-spin chemistry ?

NH_3 ortho-to-para ratio

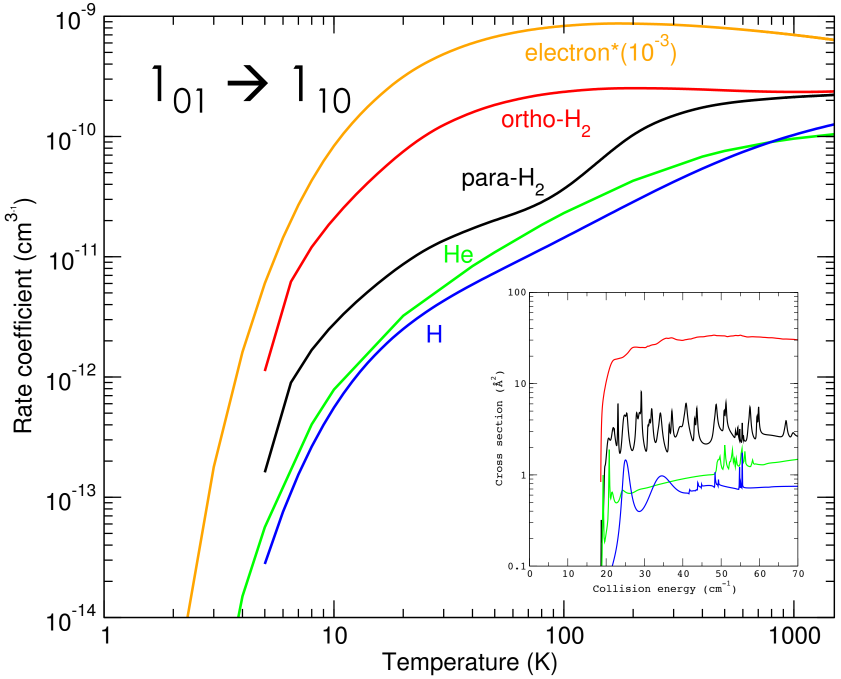


- In a pH_2 enriched gas, formation of pNH_3 is favored (Faure et al. ApJ 2013)
- This is due to nuclear-spin selection rules (Quack 1977, Oka 2004, Schmiedt et al. 2016)
- Several other hydrides expected to be sensitive to the OPR of H_2, see talk by Romane Le Gal (NH_2)

Oxygen

H_2O excitation

$H_2O(j_{kakc}) + X \rightarrow H_2O(j'_{k'ak'c}) + X$



Faure et al. (2004); Yang et al. (2013); Daniel et al. (2011); Daniel et al. (2015)

- Water has been extensively studied in collision with He, H, H_2 and e^-
- No simple scaling relationship between the various colliders
- High energy scattering is dominated by kinematics (rather than features of the PES)

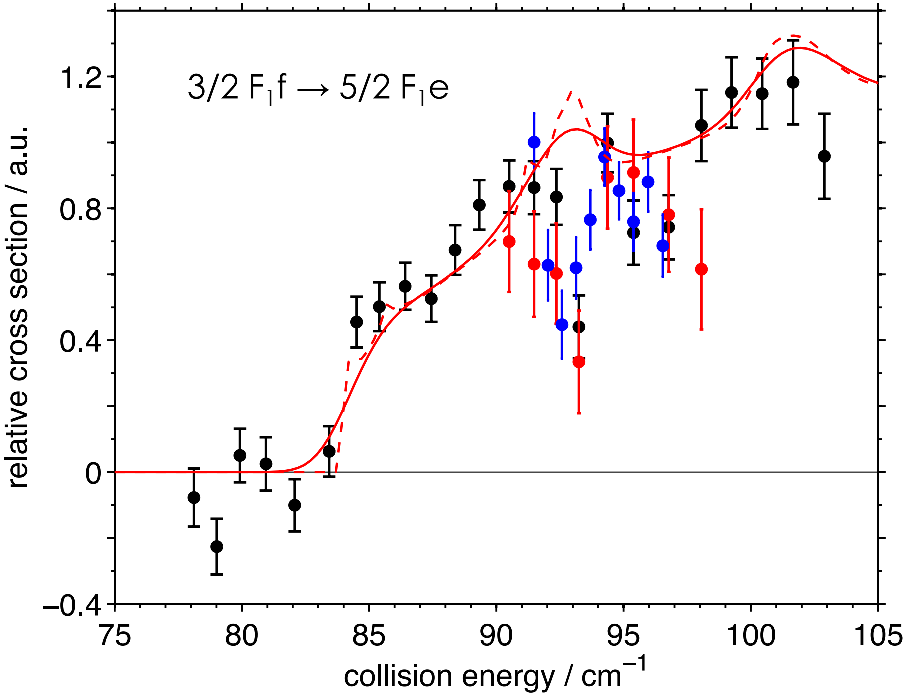
H_2O excitation

$H_2O(j_{kakc}) + H_2 \rightarrow H_2O(j'_{k'ak'c}) + H_2$

- The H_2O-H_2 PES of Valiron et al. (2008) was fully checked experimentally:
  - Inelastic differential cross
  - Pressure broadening
  - Elastic integral cross sections
  - Spectrum of the complex
  - Second virial coefficient
  - Vibrational relaxation
- Most recent check in crossed molecular beams in Bordeaux

OH excitation

OH(j) + H_2 → OH(j’) + H_2

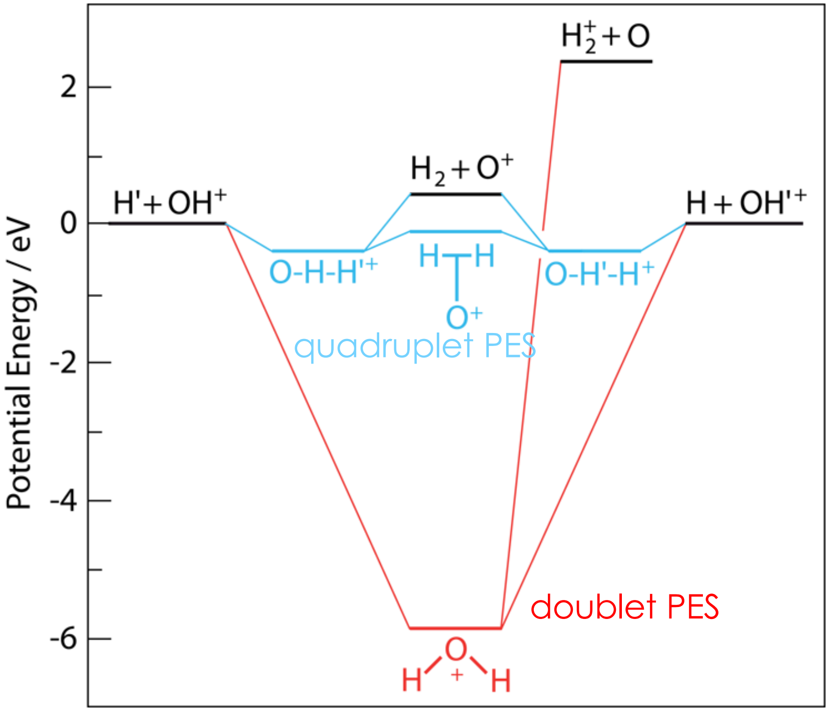


Schewe et al. J Chem Phys (2015)

- New OH-H_2 PESs obtained by Ma et al. (2014)
- In contrast to CH-H_2, there is no formation and decay of a collision complex
- Cross sections with pH_2 differ significantly from Offer et al. (1994)

OH⁺ excitation

$OH^+(j, F) + H \rightarrow OH^+(j', F') + H$



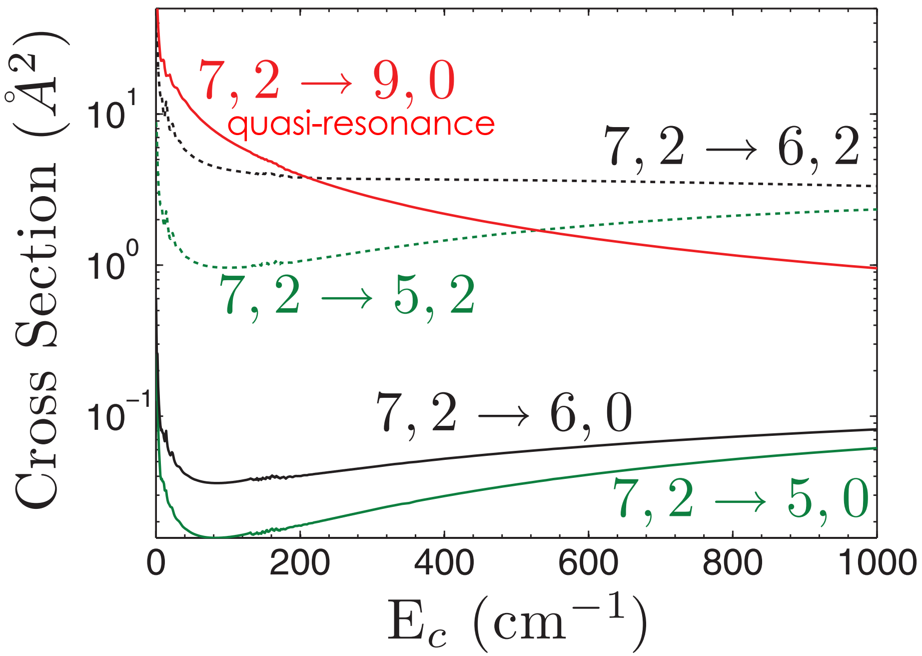
Stoecklin et al. J Phys ChemA (2015)

- The abstraction channel is closed, in contrast to $CH^+ + H$
- Rigid-rotor approximation is acceptable (Stoecklin et al. 2015), see talk by François Lique
- Electron-impact cross sections also available (van der Tak et al. 2013)

Chlorine

HCl excitation

$HCl(j) + H_2 \rightarrow HCl(j') + H_2$

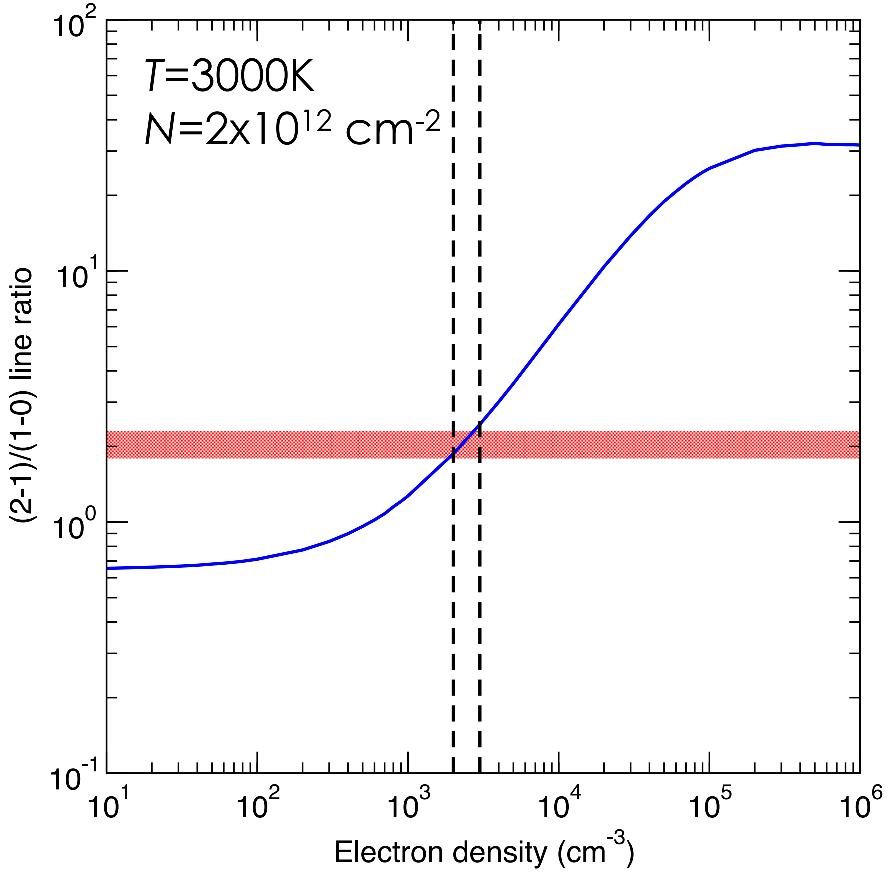


Lanza et al. J Chem Phys (2014)

- HCl expected to be the main reservoir of chlorine in dense gas
- Calculations with H_2 strongly differ from He, e.g. near-resonant energy transfer.
- From the detection in L1157-B1 (Codella et al. 2012) HCl is a negligible reservoir of chlorine

Argon

ArH$^+$ excitation



Hamilton et al. MNRAS (2016)

- ArH$^+$ first detected in the Crab nebula by Barlow et al. (2013)
- Collisions with H and H$_2$ can be neglected (Loh et al. 2012)
- Robust determination of electron density (in good agreement with S$^+$ observations)

Summary
List of available systems

	He	H_2	H	e-
CH	X	X		
CH_2	X			
CH^+	X		X	X
NH	X			
NH_2		X		
NH_3	X	X	X	
OH	X	X		
H_2O	X	X	X	X
OH^+	X		X	X
H_3O^+				X
SH	X			
HF	X	X		
HCl	X	X	X	X
ArH^+				X

- home.strw.leidenuniv.nl/~moldata/
- basecol.obspm.fr/
- ipag.osug.fr/Hydrides/

Conclusions

- Current calculations give an accuracy rivalling experiment
- Excitation of hydrides is strongly sensitive to the collider (He, pH_2, oH_2, e^-)
- State-to-state formation rates are becoming available
- Nuclear spin selection rules are crucial to model o/p ratios

Ackowledgements

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