Collisional Excitation of Interstellar Hydrides

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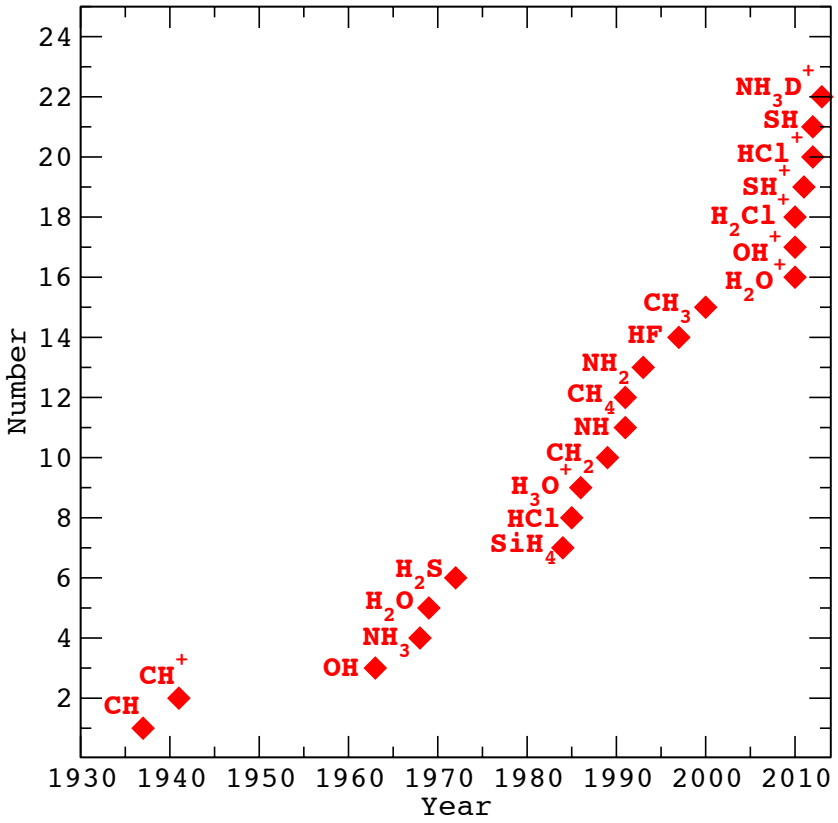
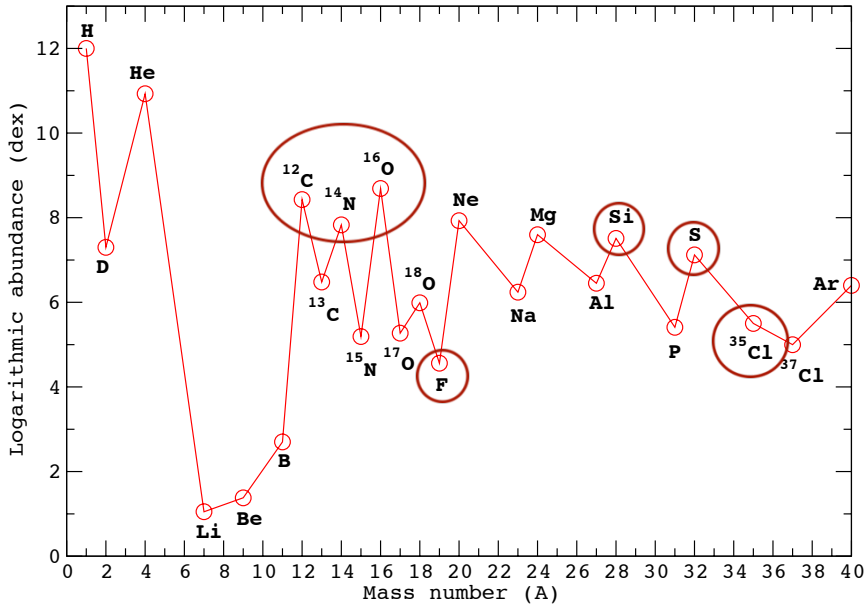
Motivation



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

- Hydrides play a central role in astrochemistry as
  - **reservoirs** of heavy elements
  - **building blocks** of chemistry
- **State-specific reactive processes** with electrons, H and H_2 compete with energy transfer processes

Outline



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

- Carbon
  - CH^+
- Nitrogen
  - NH, NH_3
- Oxygen
  - OH, OH^+, H_2O
- Halogen
  - HF, HCl

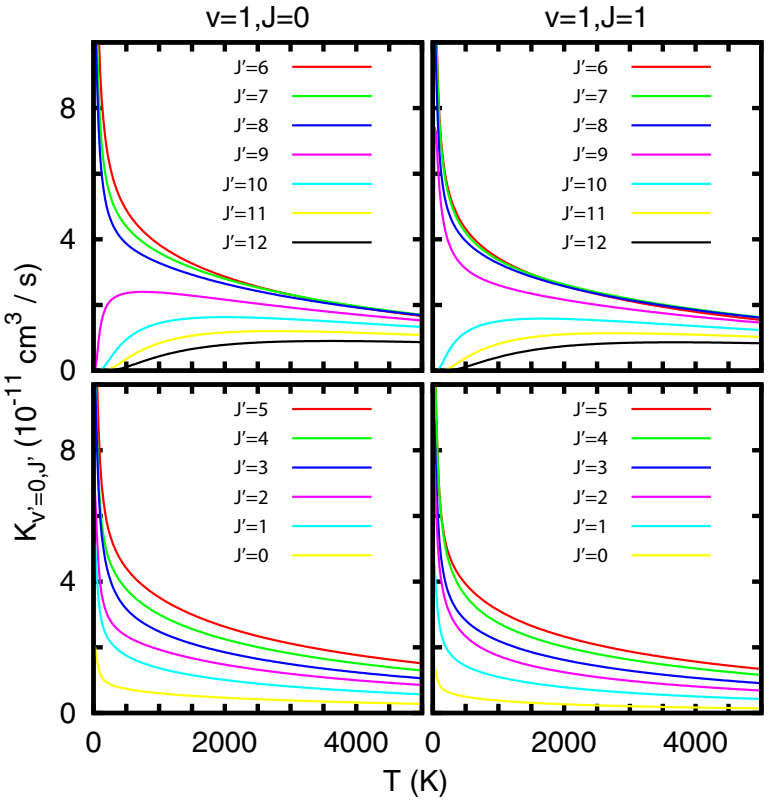
Hydride chemistry

- Initial steps
  - $X + H_2 \rightarrow XH + H$ (e.g. F or high temperature)
  - $X^+ + H_2 \rightarrow XH^+ + H_2$ (e.g. X=C, N, Cl)
  - $X + H_3^+ \rightarrow XH^+ + H_2$ (e.g. X=C, O)
- Hydrogen abstraction
  - $XH_n^+ + H_2 \rightarrow XH_{n+1}^+ + H$ (n=1-3)
- Dissociative recombination
  - $XH_n^+ + e^- \rightarrow XH_{n-1} + H$ (n=2-4)

Carbon

CH^+ formation

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

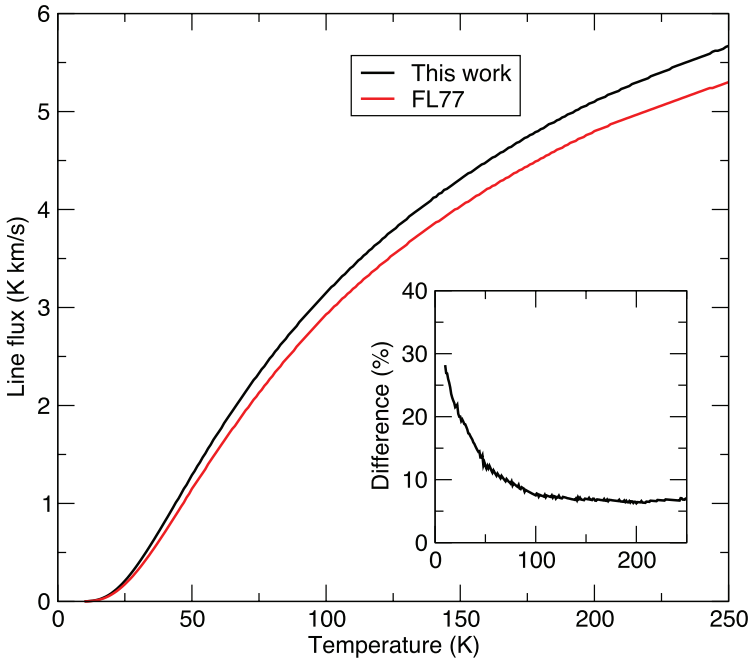


Zanchet et al. ApJ 766 80 (2013)

- Wavepacket calculations by Zanchet et al. (2013) using the PES of Stoecklin & Halvick (2005)
- In PDRs, CH^+ excitation is mostly driven by **chemical pumping** (see also Godard & Cernicharo 2013)
- Talk by B. Godard
- $C^{2+} + H_2 \rightarrow CH^+ + H^+$ recently investigated by Bacchus-Montabonel & Wiesenfeld (2013)

C^+ excitation

$C^+(^2P_j) + H_2 \rightarrow C^+(^2P_{j'}) + H_2$

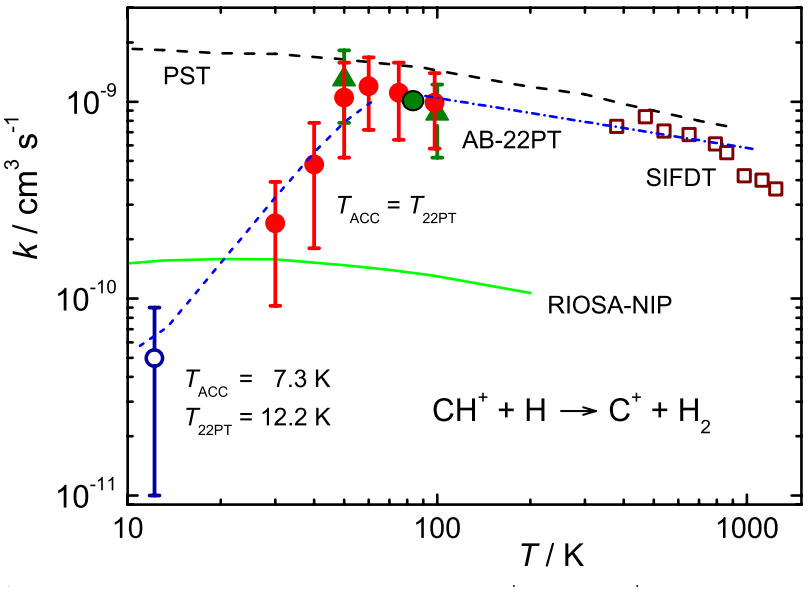


Lique et al. J. Chem. Phys. 138 204314 (2013)

- Close-coupling calculations by Lique et al. (2013) using a dedicated new PES
- The flux of the $^2P_{3/2} \rightarrow {}^2P_{1/2}$ line at 158μm is **increased by up to 30%** for typical diffuse cloud conditions

CH^+ destruction

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

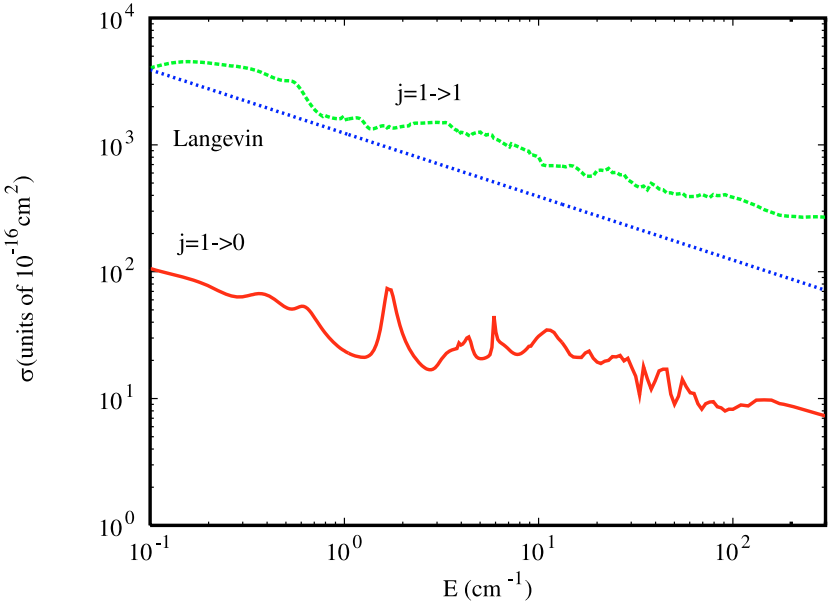


Plasil et al. ApJ 737 60 (2011)

- QCT, quantum and statistical calculations by Halvick et al. (2007), Warmbier & Schneider (2011)
- Recent measurements by Plasil et al. (2013) suggest that **non-rotating CH^+ is protected** against H attack
- **A new CH_2^+ PES** is required to interpret the 22PT measurements (see Grozdanov & McCarroll 2013)

CH^+ excitation

$CH^+(j) + He \rightarrow CH^+(j') + He$



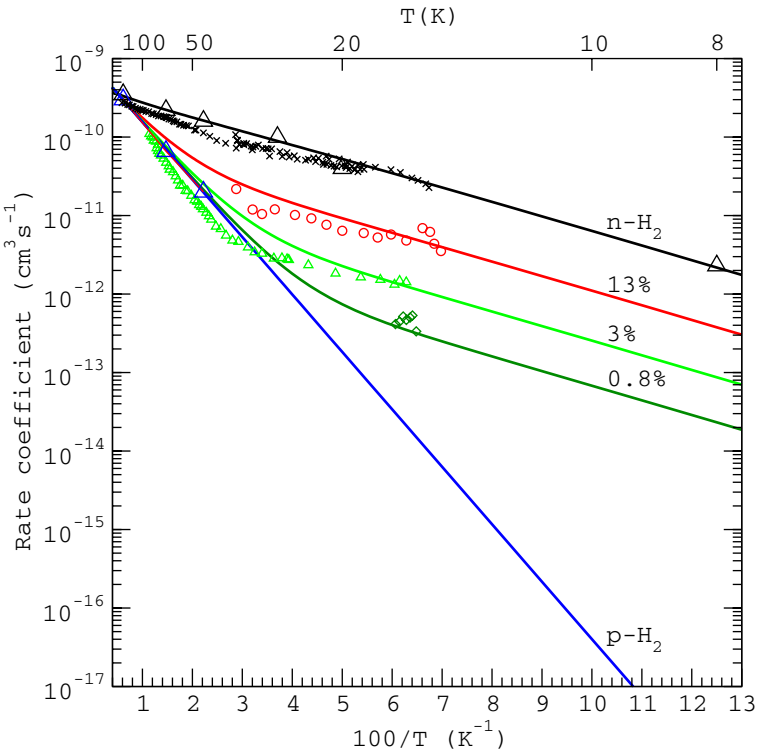
Turpin et al. ApJ 511 A28 (2010)

- Close-coupling calculations by Turpin et al. (2010) using a **non-reactive** CH^+-He PES
- Large differences expected for H and H_2, which are reactive with CH^+
- Electron-impact rate coefficients computed by Lim et al. (1999) using *R*-matrix method

Nitrogen

NH^+ formation

$N^+(^3P) + H_2(j) \rightarrow NH^+(X^2\Pi) + H$

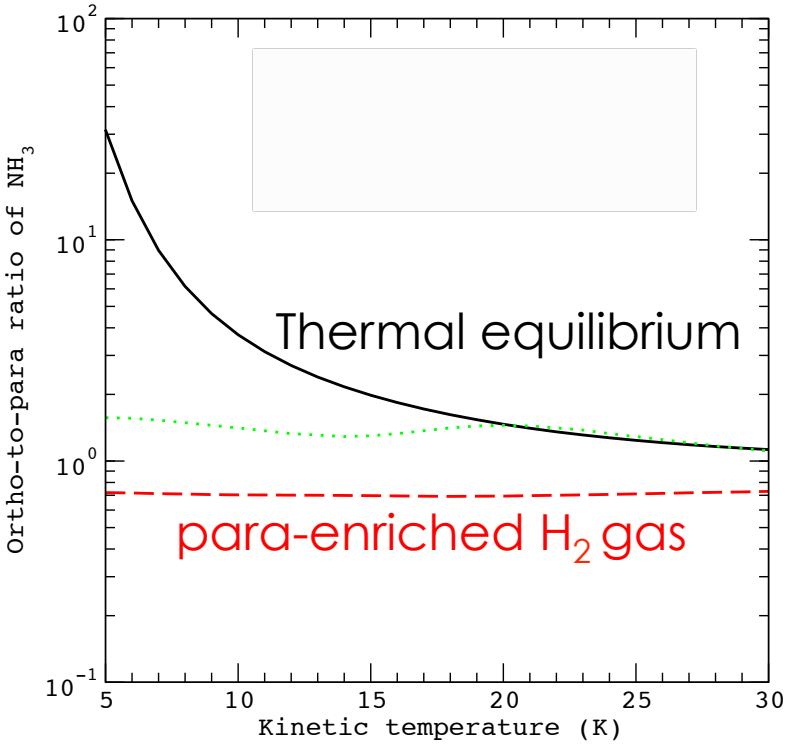


Dislaire et al. A&A 737 60 (2012)

- Pioneering measurements by Marquette et al. (1988), Gerlich (1993)
- The reaction is **endothermic or hindered** by a small barrier
- Strong dependence on the **o-H_2 fraction** and **fine structure** states of N^+ (Zymak et al. 2013)

NH_3 formation

$NH_n^+ + H_2 \rightarrow NH_{n+1}^+ + H$ (n=0-3); $NH_4^+ + e^- \rightarrow NH_3 + H$

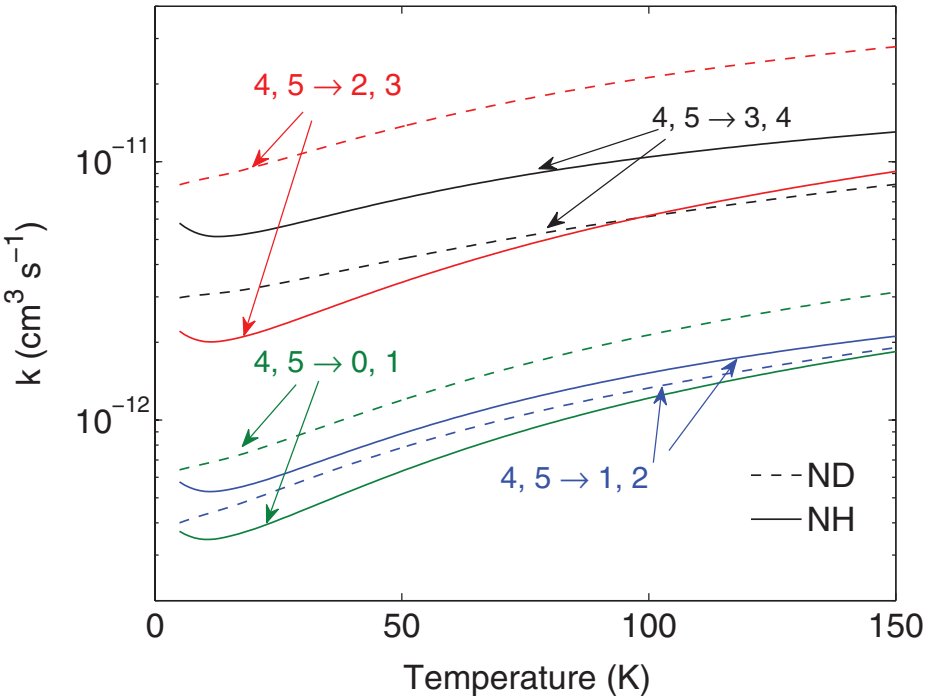


Faure et al. ApJ 770 L2 (2013)

- Surprising low values of the **NH_3 o/p ratio (<1)** measured by Herschel (Persson et al., Le Gal et al.)
- A low o/p ratio for NH_3 is consistent with **nuclear spin selection rules** in a para-enriched H_2 gas
- Supports a gas-phase synthesis
- See Talk by C. Persson, Poster by R. Le Gal P68,

NH excitation

NH(N, j, F_1, F)+He → NH(N', j', F_1', F')+He

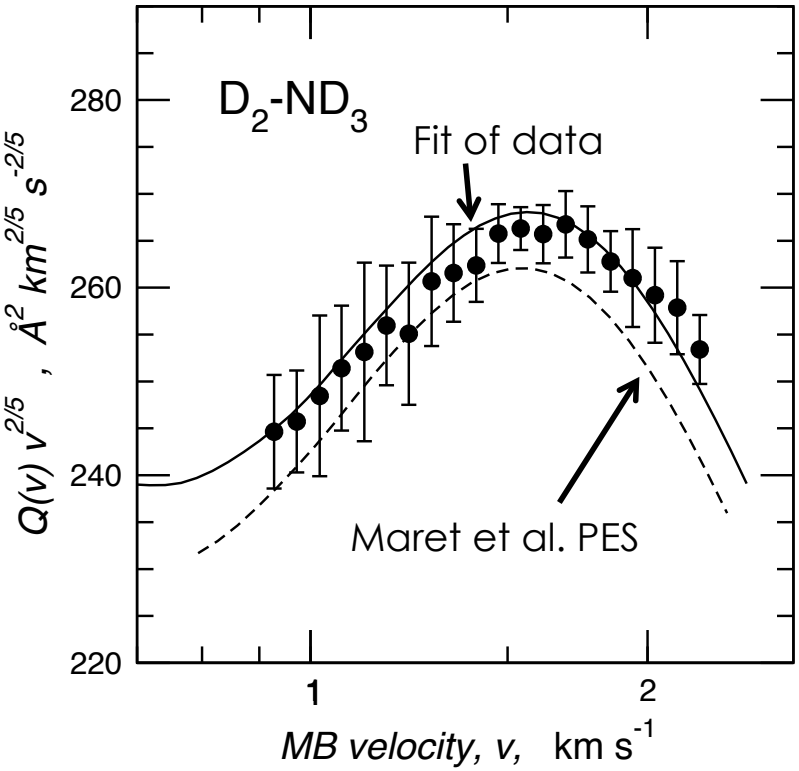


Dumouchel et al. J. Chem. Phys. 137 114306 (2012)

- **H/D isotopic substitution** has strong effects for hydrides
  - kinematics (mass and velocities)
  - PES (centre of mass, intramolecular geometries)
- See also Scribano et al. (2010), Wiesenfeld et al. (2011) for HDO and D_2O

NH_3 excitation

$NH_3(j_k) + H_2 \rightarrow NH_3(j'_{k'}) + H_2$



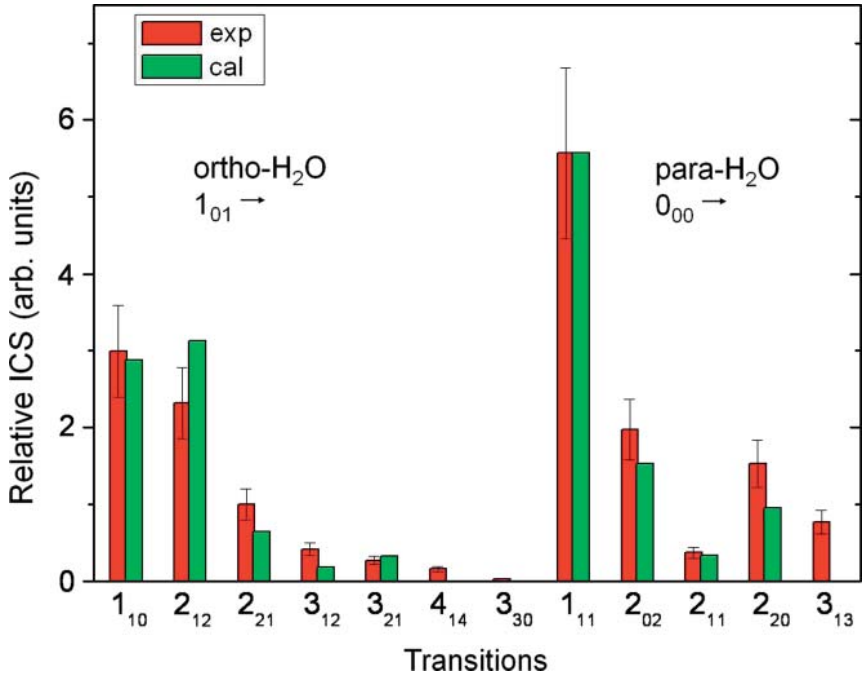
Pirani et al. submitted to JPCA

- Close-coupling calculations by Maret et al. (2009) using a high-accuracy PES
- Non-LTE calculations suggests that the calibration of **ammonia thermometer is robust**
- The accuracy of the PES was recently confirmed by molecular beam experiment

Oxygen

H_2O excitation

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

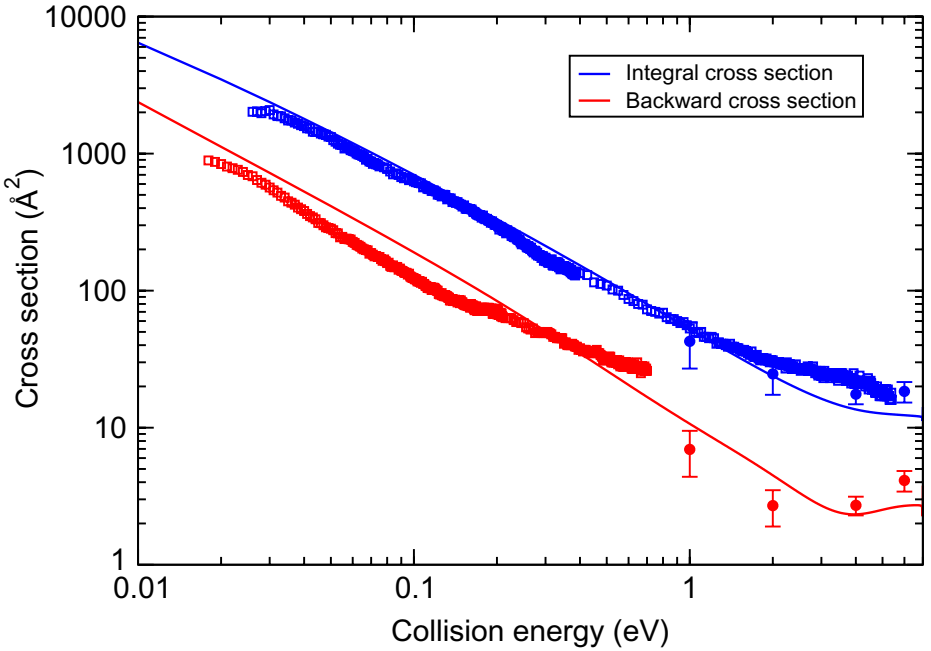


Yang et al. J. Chem. Phys. 134 204308 (2011)

- The high accuracy of the H_2O-H_2 PES (Valiron et al. 2008) was confirmed experimentally:
  - **Inelastic differential cross**
  - Pressure broadening
  - Elastic integral cross sections
  - Spectrum of the complex
  - Second virial coefficient
  - Vibrational relaxation
- See Daniel et al. 536 A76 A&A (2011)
  (high temperature : Faure & Josselin 492 257 2008)

H_2O excitation

$H_2O(j_{kakc}) + e^- \rightarrow H_2O(j'_{ka'kc'}) + e^-$

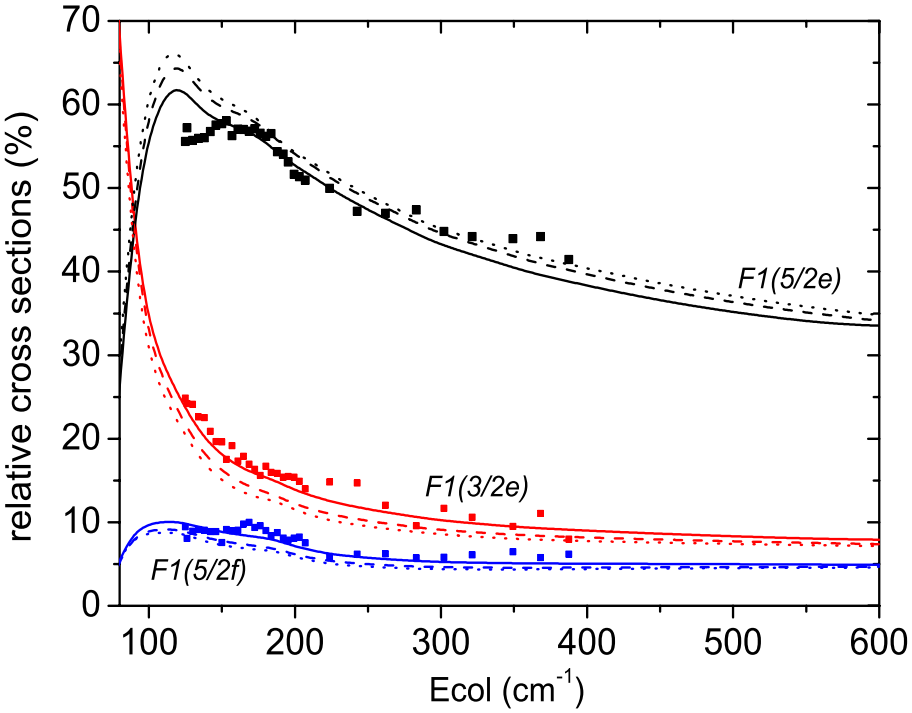


Zhang et al. Phys. Scr. 80 015301 (2009)

- *R*-matrix calculations by Faure et al. (2004) were validated by differential/integral measurements
- Electron-impact excitation of water is crucial as soon as $\mathbf{x_e > 10^{-5}}$ (e.g. PDRs, comets)

OH excitation

$OH(F_i, j) + He \rightarrow OH(F'_i, j') + He$

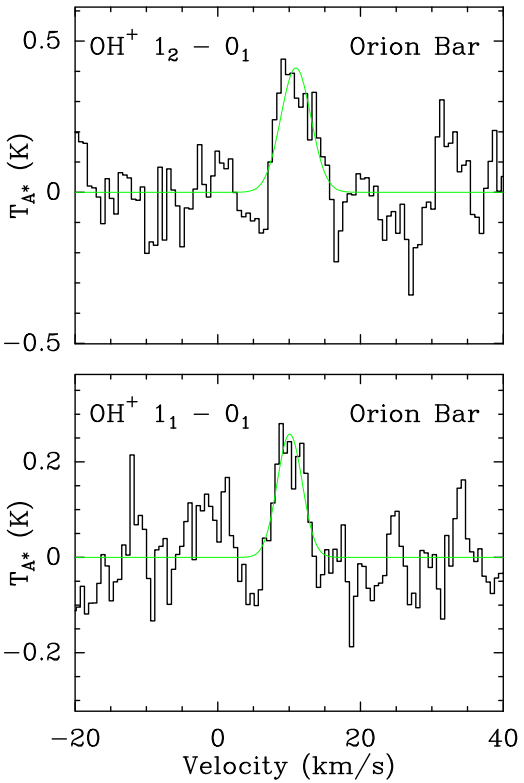


Kalugina et al. in preparation

- Rotationally inelastic scattering of OH by He and D_2 was measured by Kirste et al. (2010)
- Excellent **agreement between theory and experiment** with the new OH-He PES (Kalugina et al.)
- Different propensity rules predicted for H_2 collisions (Alexander et al.)

OH^+ excitation

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

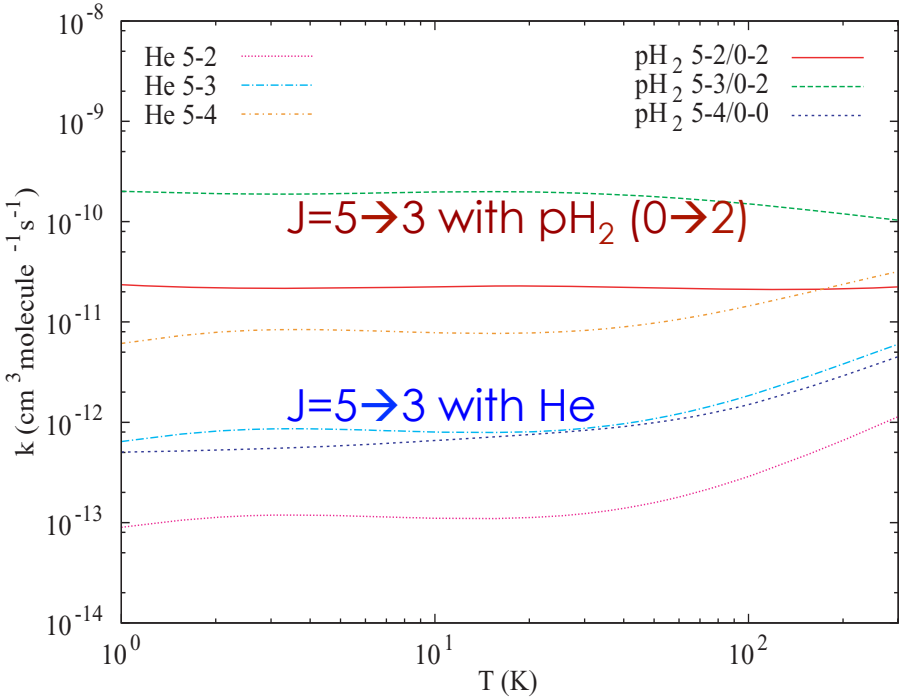


van der Tak et al. submitted

- Talk by Z. Nagy
- Close-coupling calculations by Lique et al. (in preparation), including hyperfine structure
- **Large differences expected for H**
- Electron-impact excitation computed by van der Tak et al. (submitted) using Coulomb-Born

Fluorine
Chlorine

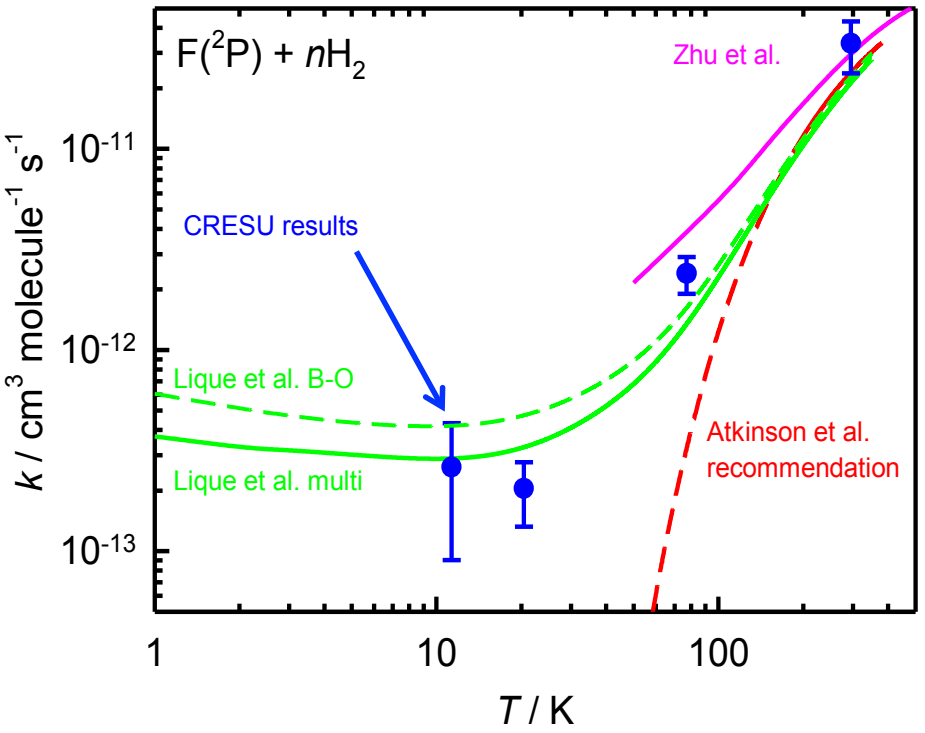
HF and HCl excitation



Guillon & Stoecklin MNRAS 420 579 (2012)

- Close-coupling calculations on
  - HF+H_2 by Guillon & Stoecklin (2012)
  - HCl+H_2 by Lanza et al. (in prep.)
- Significant **differences between He and p-H_2**, in particular near-resonant energy transfer.
- See Poster on Cl by M. Kama P71
- Electron-impact excitation of HF computed in van der Tak et al. (2012)

HF formation



Tizniti et al., submitted

- **CRESU measurements down to 11K** have confirmed the quantum calculations of Lique et al. (2011)
- Non-adiabatic effects important
- Strong non-Arrhenius temperature dependence (tunneling)

Conclusions

- Excitation of hydrides is strongly **sensitive to the collider** (He, pH_2, oH_2)
- **Chemical pumping** important for reactive ions (state-specific rates essential)
- **Nuclear spin selection rules** crucial to predict o/p ratios
- Strong effects of **H/D substitution**
- Current quantum calculations give an **accuracy rivalling experiment**

- Systems studied include:
  - CH^+
  - NH, ND
  - NH_3, ND_2H
  - OH, OH^+, H_2O, HDO, D_2O
  - HF
  - HCl
- Future systems include:
  - CH
  - NH_2D
  - H_3O^+
  - SH^+
  - …

Ackowledgements

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  - Agence Nationale de la Recherche (ANR-HYDRIDES, contract ANR-12-BS05-0011-01) http://ipag.osug.fr/Hydrides/
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  - "Région Rhône-Alpes" (Cible program)