Collisional Excitation of Interstellar Hydrides

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Motivation

- 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

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

- Carbon
- CH⁺
- Nitrogen
- NH, NH₃
- Oxygen
- OH, OH⁺, H₂O
- Halogen
- HF, HCl

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

\[ \text{C}^+(2\text{P}) + \text{H}_2(\nu, j) \rightarrow \text{CH}^+(X^1\Sigma^+, j') + \text{H} \]

- 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**

\[ \text{C}^+ (2P_j) + \text{H}_2 \rightarrow \text{C}^+ (2P_j') + \text{H}_2 \]

- 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 158\( \mu \)m is **increased by up to 30%** for typical diffuse cloud conditions

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**CH$^+$ destruction**

\[ \text{CH}^+ (^1\Sigma^+) + \text{H} \rightarrow \text{C}^+ (^2\Pi) + \text{H}_2 \]

- 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**

\[
\text{CH}^+(j) + \text{He} \rightarrow \text{CH}^+(j') + \text{He}
\]

- Close-coupling calculations by Turpin et al. (2010) using a non-reactive CH⁺-He PES
- Large differences expected for H and H₂, which are reactive with CH⁺
- Electron-impact rate coefficients computed by Lim et al. (1999) using R-matrix method
NH\(^+\) formation

\[ \text{N}^+(3\text{P}) + \text{H}_2(\text{j}) \rightarrow \text{NH}^+(X^2\Pi) + \text{H} \]

- 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)
NH₃ formation

NHₙ⁺+H₂ → NHₙ₊₁⁺ + H (n=0-3); NH₄⁺ + e⁻ → NH₃ + H

- Surprising low values of the NH₃ o/p ratio (<1) measured by Herschel (Persson et al., Le Gal et al.)
- A low o/p ratio for NH₃ is consistent with nuclear spin selection rules in a para-enriched H₂ gas
- Supports a gas-phase synthesis
- See Talk by C. Persson, Poster by R. Le Gal P68,

NH excitation

\[ \text{NH}(N, j, F_1, F) + \text{He} \rightarrow \text{NH}(N', j', F_1', F') + \text{He} \]

- **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\(_2\)O

**NH$_3$ excitation**

$\text{NH}_3(j_k) + \text{H}_2 \rightarrow \text{NH}_3(j'_{k'}) + \text{H}_2$

- 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

**Graph:**

- **Axes:**
  - **Y-axis:** $Q(v)v^{2/5}$, $\AA^2$ km$^{-2/5}$ s$^{-2}$
  - **X-axis:** MB velocity, $v$, km s$^{-1}$

- **Label:** Pirani et al. submitted to JPCA
Oxygen
**H$_2$O excitation**

$\text{H}_2\text{O}(j_{\text{kakc}}) + \text{H} \rightarrow \text{H}_2\text{O}(j'_{\text{k'ak'c}}) + \text{H}$

- The high accuracy of the H$_2$O-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)

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![Graph showing relative integral cross sections for transitions](image)

$H_2O$ excitation

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

- R-matrix calculations by Faure et al. (2004) were validated by differential/integral measurements

- Electron-impact excitation of water is crucial as soon as $x_e > 10^{-5}$ (e.g. PDRs, comets)
OH excitation

\[ \text{OH}(F_i, j) + \text{He} \rightarrow \text{OH}(F'_i, j') + \text{He} \]

- 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

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

- 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

van der Tak et al. submitted
Fluorine
Chlorine
HF and HCl excitation

- Close-coupling calculations on
  - HF+H₂ by Guillon & Stoecklin (2012)
  - HCl+H₂ by Lanza et al. (in prep.)

- Significant differences between He and p-H₂, 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

- 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, pH₂, oH₂)
- 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
  - NH₃, ND₂H
  - OH, OH⁺, H₂O, HDO, D₂O
  - HF
  - HCl

- Future systems include:
  - CH
  - NH₂D
  - H₃O⁺
  - SH⁺
  …
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